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Mercury pollution in fish and invertebrates in natural and wildfire impacted lakes in Norway

Telemark University College
Faculty of Arts and Sciences

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Thesis for the degree of Doctor Philosophiae

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Be bold and jump in that lake, go climb that tree to see the world… your life will be richer!

Let’s give thanks for the good things in life ☺

Bø i Telemark
June, 2014

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Summary

Mercury (Hg) contamination in fish has become a global issue and remains a major problem of concern in the Nordic countries, with atmospheric long-range transport of Hg being the main source to aquatic ecosystems. Most Hg in fish is present as monomethylmercury (CH_3Hg^+, MeHg), a powerful neurotoxin that biomagnifies to harmful concentrations through the aquatic food web, and is mainly obtained from the diet.

The main goal of this dissertation was to investigate the Hg content in fish from lakes with different environmental characteristics, including both natural and wildfire impacted lakes, and to discuss different factors affecting the Hg content in biota. The fieldwork of this thesis was conducted in several lakes: two relatively big lakes in Telemark county (Lake Norsjø and Lake Heddalsvatn) and in nine small boreal acidic lakes located in a wildfire impacted area in Mykland, southern Norway. Hg concentrations were investigated in various fish species as well as in macroinvertebrates. In addition, stable isotope analysis of carbon and nitrogen ($\delta^{13}C$ and $\delta^{15}N$) were measured in fish and macroinvertebrates. The $\delta^{15}N$ signatures were used for estimates of trophic position, while the $\delta^{13}C$ signatures were used to estimate the relative contribution of food derived from littoral or pelagic habitats. For the wildfire study, water samples were collected monthly over four years and analyzed for the main water chemical parameters. Fish were also sampled during 2008, 2010 and 2012 to evaluate potential year differences on Hg, $\delta^{13}C$ and $\delta^{15}N$.

Food web transfer of total Hg (THg) was studied using trophic magnification slopes (TMS), i.e. slopes of the linear regression between log-transformed Hg and relative trophic position (stable nitrogen isotope, $\delta^{15}N$) in biota, and used as indicators of the biomagnifying potential of Hg in different aquatic ecosystems. The TMS values ranged from 0.16 to 0.25 and varied depending on the ecosystem characteristics and physico-chemical parameters such as temperature related processes, total organic carbon (TOC) or pH. These values indicated trophic magnification factors of Hg ranging from 3.6 to 7.1 per trophic level.

Seasonal variations of Hg concentrations were investigated in Lake Heddalsvatn during December, May and September, in three fish species. Results showed that there were seasonal differences, but the causes varied depending on the fish species. Fish caught in December (European whitefish, *Coregonus lavaretus*; northern pike, *Esox lucius*) had the highest Hg concentrations, while the concentrations in May were higher than in September for all three

species, statistically significant ($p < 0.0001$) for European perch (*Perca fluviatilis*) and close to significant for pike ($p = 0.07$). Somatic growth dilution was the most likely explanation for the perch population, whereas for whitefish and pike this mechanism could not be the explanatory factor as there was no measurable growth from May to September.

We used the $\delta^{13}C$ signatures of primary consumers from pelagic and littoral habitats in a simple two-source mixing model to estimate the relative dietary contribution in fish from food derived from the littoral or pelagic habitats in Lake Norsjø. Perch exhibited the highest zoobenthos reliance (89 ± 14%), while European smelt (*Osmerus eperlanus*) exhibited the lowest (37 ± 7%). The most intermediate $\delta^{13}C$ signatures, i.e. supported by a mixed diet of littoral and pelagic food webs, were found in piscivore species with the highest trophic position, and the subsequent highest Hg concentrations both in Lake Norsjø and Lake Heddalsvatn.

The changes in water chemistry in the wildfire affected area were studied for over 4 years (2008-2012) following the fire. There were large lake-to-lake variations and hydrological conditions such as heavy rain or snowmelt periods were the main reason for the most severe water chemical episodes. There was an initial drop in the acid neutralizing capacity (ANC) of the lakes two months after the fire, due to a faster mobilization of sulfate and chloride ions compared to base cations. An initial decrease in TOC and increase in nutrient runoff (nitrogen, N, and phosphorous, P) were observed in the initial post-fire period, followed by a gradual decrease in N and P, and increases in TOC. The water chemical conditions were almost re-established one year after the wildfire and had almost returned to pre-fire levels four and a half years after the fire.

A water survey analysis was conducted in June 2012, four years after the fire, and the concentrations of THg and MeHg ranged between 1.17 - 2.63 ng L^{-1} and 0.053 - 0.188 ng L^{-1}, respectively. Both variables were strongly and positively correlated to TOC and TOC-related variables such as color or UV absorbance, and with total-P and total iron. MeHg was also positively correlated with total-N and chlorophyll-*a*.

There was no conclusive evidence that the fire affected the Hg concentrations in fish, but generally higher levels were found two years after the fire. Increased nutrients and chlorophyll-*a* concentration in the lakes might be key factors to explain this increment. Natural factors as year-to-year variations in thermocline depth or suboxic status in lakes make it difficult to draw any strong conclusions about direct wildfire effects on Hg in the biota from the investigated lakes.

Sammendrag

Høye kvikksølvkonsentrasjoner (Hg) i mange fiskearter er et globalt problem, da det blant annet medfører begrensninger for salg og konsum av flere arter både i ferskvann og saltvann. For ferskvannsfisk i Skandinavia skyldes dette primært en kombinasjon av vannkjemiske forhold, spesielt i våre skog- og myrpåvirkede innsjøer, og betydelig tilførsler av langtransportert Hg via atmosfæren. I hovedsak forkommer Hg som monometyl-Hg (CH_3Hg^+, MeHg) i fiskekjøtt. Dette er en nevrotoksisk forbindelse som oppkonsentreres i næringskjeden, og derfor kan medføre svært høye konsentrasjoner i toppredatorer som fiskespisende fisk, fugl og pattedyr, inkludert menneske. I hovedsak kommer MeHg inn i organismene via maten de spiser.

Hovedmålet for avhandlingen har vært å undersøke Hg-konsentrasjoner i fisk i innsjøer med ulike fysisk-kjemiske forhold, og både naturlige og brannpåvirkede innsjøer har blitt undersøkt for å diskutere ulike faktorer som kan være avgjørende for Hg-nivåene i ulike akvatiske næringskjeder. Feltarbeidet har vært gjennomført i to store innsjøer i Telemark (Norsjø og Heddalsvatn), samt i ni mindre boreale, sure innsjøer i et brannpåvirket område på Sørlandet (Mykland). I alle innsjøene har Hg-konsentrasjonene i fisk og akvatiske invertebrater (zooplankton og bunndyr) blitt undersøkt. I tillegg er det gjennomført stabile isotopanalyser av karbon ($\delta^{13}C$) og nitrogen ($\delta^{15}N$) i organismene. Mens $\delta^{15}N$ -signaturen i en organisme kan si noe om organismens trofiske posisjon (hvor i næringskjeden den befinner seg), vil dens $\delta^{13}C$-signatur kunne si noe om hva slags mat organismen primært spiser, det vil si om de primært lever av bunndyr i strandsonen (littoral føde) eller av zooplankton som befinner seg ute i de frie vannmassene (pelagisk føde). I brannområdet ble også hver måned gjennomført makrokjemiske analyser av innsjøene over en fire-års periode (2008-2012). Tre ganger under den samme tidsperioden (høsten 2008, 2010 og 2012) ble prøver av fisk tatt for å kunne vurdere mulige endringer i Hg-nivåer og/eller $\delta^{15}N$ og $\delta^{13}C$ signaturer som en følge av brannen.

Oppkonsentreringen av Hg gjennom næringskjeden ble kvantifisert med en trofisk magnifiserings-koeffisient (TMS = Trophic Magnification Slope). TMS-verdien er stigningskoeffisienten for den lineære regresjonen mellom log-transformert Hg-konsentrasjon og relativ trofisk posisjon ($\delta^{15}N$) for de ulike organismene i hver enkelt innsjø. I de ulike innsjøene varierte TMS-verdiene varierte mellom 0.16 – 0.25. Ulike nedbørsfelt-spesifikke forhold og fysisk-kjemiske forhold i innsjøene, som vanntemperatur, konsentrasjon av totalt organisk karbon

(TOC) og pH, var sentrale forklaringsfaktorer for variasjonene i innsjøenes TMS-verdi. Variasjonene i TMS (0.16 – 0.25) betyr forskjeller i oppkonsentreringsfaktor for Hg gjennom næringskjeden fra 3.6 til 7.1 per trofisk nivå i de undersøkte innsjøene.

For å studere mulige sesongvariasjoner i Hg-konsentrasjoner gjennom året, ble fisk undersøkt i mai, september og desember i innsjøen Heddalsvatn. Resultatene dokumenterte sesongvariasjoner, men årsakene til disse varierte mellom de undersøkte fiskeartene, sik (*Coregonus lavaretus*), gjedde (*Esox lucius*) og abbor (*Perca fluviatilis*). Fisk fanget i desember (sik og gjedde) hadde de høyeste Hg-konsentrasjonene, mens konsentrasjonene i mai var høyere enn i september for alle tre fiskearter, statistisk signifikant ($p < 0.0001$) for abbor og tilnærmet signifikant for gjedde ($p = 0.07$). Somatisk vekstfortynning var den mest sannsynlige årsaken til lavere Hg-konsentrasjon i abbor i september i forhold til i mai. For sik og gjedde måtte det være andre årsaker til lavere konsentrasjoner i september enn i mai, siden vi ikke kunne dokumentere noen målbar vekst fra mai til september i det innsamlede prøvematerialet.

Ved å benytte $\delta^{13}C$ signaturene til pelagiske og littorale primærkonsumenter kan en ved bruk av en enkel to-komponent blandingsmodell, estimere hvor mye av dietten til hver enkelt fisk som kommer fra de to «hovedmatkildene» i innsjøen. Denne modellen ble anvendt i innsjøen Norsjø, og viste at abbor var den fiskearten som i størst grad (89 ± 14 %) hentet sin føde fra littoralsonen (bunndyr i strandsonen), mens krøkle (*Osmerus eperlanus*) var den undersøkte fiskearten som hadde minst innslag av littoral føde (37 ± 7 %). Mest intermediære $\delta^{13}C$ signaturer ble påvist i fiskespisende fisk. Disse fiskene befant seg også høyest oppe i næringskjeden (høyest $\delta^{15}N$-signaturer) og hadde derfor også de høyeste Hg-konsentrasjonene. Dette ble også dokumentert i Heddalsvatn.

I brannområdet i Mykland ble vannkjemiske effekter i innsjøene undersøkt i fire år etter brannen (2008-2012). Det var store variasjoner mellom innsjøene med hensyn til vannkjemiske effekter av brannen, men for alle innsjøene ble de mest ekstreme vannkjemiske episodene påvist under hydrologiske episoder som intensive regn- og snøsmeltingsperioder. Under en betydelig nedbørsepisode cirka to måneder etter brannen, ble det påvist en kraftig nedgang i syrenøytraliseringskapasiteten (ANC) til innsjøene, som en følge av betydelig raskere mobilisering av sulfat- og kloridioner fra nedbørsfeltene og ut i innsjøene i forhold til mobiliseringen av basekationer. Samtidig var det en nedgang i konsentrasjonen av totalt organisk karbon i innsjøene, mens konsentrasjonene av næringsstoffer som nitrogen (N) og fosfor (P) økte i innsjøene. Etter disse til dels betydelige vannkjemiske endringene under en relativt kort periode etter brannen, normaliserte vannkjemien seg relativt godt i løpet av det første året, og fire og et halvt år etter brannen, var forholdene tilnærmet slik de var før brannen.

I juni 2012, fire år etter brannen, ble det gjennomført undersøkelser av total Hg (THg) og MeHg-konsentrasjoner i innsjøene. Konsentrasjonene av THg varierte mellom 1.17 – 2.63 ng L^{-1} mens konsentrasjonene av MeHg varierte mellom 0.053 – 0.188 ng L^{-1}. Begge Hg-variablene var sterkt positivt korrelert med TOC-konsentrasjonen i innsjøene og andre TOC-relaterte variabler som farge og UV-absorbans. Signifikante positive korrelerasjoner ble også funnet mellom THg/MeHg og total-P og total-Fe. MeHg var i tillegg signifikant positivt korrelert med total-N og klorofyll-*a*.

Det var ingen entydig tendens til at brannen hadde påvirket Hg-konsentrasjonene i fisk, men generelt ble det funnet høyere Hg-konsentrasjoner i fisk to år etter brannen. Økte konsentrasjoner av næringsstoffer og klorofyll- *a* kan være mulige faktorer som kan forklare denne økningen, men naturlige år-til-år variasjoner i termoklindyp eller oksygenstatus i innsjøene gjør det vanskelig og trekke klare konklusjoner omkring direkte effekter av brannen på Hg-nivåene i akvatiske organismer i de undersøkte innsjøene.

List of papers

Paper I.

Lydersen, E. and Moreno, C. Variations in feeding habitats and mercury levels in fish from Lake Norsjø, southern Norway. Submitted.

Paper II.

Moreno, C., Fjeld, E., Deshar, M. and Lydersen, E. 2015. Seasonal variation of mercury and $\delta^{15}N$ in fish from Lake Heddalsvatn, southern Norway. *Journal of Limnology* 74(1): 1-

Paper III.

Moreno, C., Fjeld, E. and Lydersen, E. The effects of wildfire on mercury in water and biota of small boreal, acidic lakes in southern Norway. Submitted.

Paper IV.

Lydersen, E., R. Høgberget, C. Moreno, Ø. Garmo, and P. Hagen. 2014. The effects of wildfire on the water chemistry of dilute, acidic lakes in southern Norway. *Biogeochemistry* 119: 109-124

1. INTRODUCTION

Mercury (Hg) remains an environmental concern in many parts of the world as a pollutant in terrestrial and aquatic ecosystems. The contamination of fish with monomethylmercury, CH_3-Hg^+ (MeHg), the most toxic aquatic form of Hg and readily accumulated in biota, poses a human health risk. Its toxicity affects the nervous and endocrine system of fish, birds, and mammals, including humans. MeHg is readily absorbed from the gastrointestinal tract, it enters the blood, and is then distributed to all the organs including the brain (Clarckson and Magos, 2006). In the Nordic countries, the long-range transboundary transport of atmospheric Hg is the main source to ecosystem contamination (Rognerud and Fjeld, 1993; Munthe et al., 2004). The high Hg concentrations observed in Arctic biota have been hypothesized to be due to recent changes in the Hg cycle, caused by industrialization and climate change (Stern et al., 2012). However, the level of Hg pollution in fish does not only depend on the Hg input but also on external factors influencing its transport and transformation to chemical forms as MeHg (Ullrich et al., 2001).

1.1 Sources of mercury

The Hg present in the environment comes from both natural and anthropogenic sources. Hg is an element naturally present in the earth's crust, most often found in the form of cinnabar, a Hg sulfide mineral (HgS). It is also present as an impurity in valuable minerals, such as non-ferrous metals or fossil fuels (coal, in particular). Various natural processes such as volcanic eruptions and seismic activities, forest fires, weathering of Hg-containing rocks, and volatilization from the ocean can release Hg into the atmosphere, water bodies and soils. Thus, there are many natural sources of Hg which have background environmental levels that have been present since long before humans appeared (UNEP, 2013). According to Pirrone et al. (2010), the global Hg emissions by natural sources (primary Hg emissions and re-emissions) estimated for 2008, reach a total of 5207 tons yr^{-1}(Table 1), amounting to nearly 70% of the THg emissions (natural and anthropogenic) in 2008.

The anthropogenic emissions have increased dramatically during the last 150 years, i.e. from the beginning of the industrial revolution until today (AMAP, 2011). Atmospheric emissions are the most important anthropogenic source of Hg inputs to land and oceans. According to Pirrone et al. (2010), the most important anthropogenic sources are: coal and oil combustion, artisanal and small-scale gold mining, non-ferrous metal production, cement production, waste disposal and caustic soda production (Table 2). The total anthropogenic Hg emissions in 2008, 2320 tons yr^{-1}, amount to ≈ 31% of the total global Hg emissions.

Table 1 *Global Hg emissions by natural sources estimated for 2008 (Pirrone et al., 2010).*

Natural sources	**Hg (tons yr^{-1})**
Oceans	2682
Biomass burning	675
Desert/metalliferous/non-vegetated zones	546
Tundra/grassland/savannah/prairie/chaparral	448
Forests	342
Evasion after Hg depletion events	200
Agricultural areas	128
Lakes	96
Volcanoes and geothermal areas	90
Total	5207

Table 2 *Global Hg emissions by anthropogenic sources estimated for 2008 (Pirrone et al., 2010).*

Anthropogenic sources	**Hg (tons yr^{-1})**
Coal and oil combustion	810
Artisanal gold mining production	400
Non-ferrous metal production	310
Cement production	236
Waste disposal	187
Caustic soda production	163
Mercury production	50
Pig iron and steel production	43
Coal bed fires	32
Vinyl chloride monomer production	24
Other	65
Total	2320

Several countermeasures have been implemented in many countries, including Norway, in order to reduce the anthropogenic Hg emissions. The Norwegian Hg releases to air, soil and water were estimated at almost 6 tons in 1985 and 2.5 tons in 1995, but between 1995 and 2008, they were reduced by 64% to about 0.9 tons, while the target goal is a total elimination of local emission sources by 2020 (Klif, 2010). The Norwegian Hg emissions to air in 2008 were about

0.7 tons, considerably less than the atmospheric transport of Hg to Norway from other countries. Approximately, 2.6 tons of Hg are transported to Norway from sources outside the Norwegian borders (Berg et al., 2006). Thus, national emissions correspond to 27% of the total atmospheric Hg in Norway.

1.2 Mercury species

Inorganic Hg might occur in 3 valence states, elemental Hg (Hg^0), monovalent or mercurous Hg (Hg_2^{2+}), and divalent or mercuric Hg (Hg^{2+}). These cationic forms may complex with many inorganic and organic ligands, with various physical and chemical properties, decisive for mobilization and toxicity in ecosystems (Clarkson and Magos, 2006; Morel et al., 1998; AMAP, 2011). Important Hg species are:

- **Elemental Hg (metallic Hg, Hg^0).** It is the pure inorganic form, present as liquid at room temperature and evaporates slowly as Hg^0, often termed gaseous elemental mercury (GEM). The GEM dissolves rapidly in water, often termed dissolved gaseous mercury (DGM).

- **Inorganic Hg cations.** The divalent and monovalent cationic forms of Hg form various salts, primarily with inorganic anions as sulfide (S^{2-}), chloride (Cl^-) and oxide (O^{2-}), where the most common compounds found in nature are: mercuric sulfide (HgS, cinnabar), mercuric oxide (HgO) and mercuric chloride ($HgCl_2$).

- **Organic Hg.** Inorganic cationic Hg might form many complexes with organic C. The predominant form is monomethylmercury (CH_3Hg^+ or MeHg), one of the most toxic forms as it strongly binds to the sulfur-containing amino acids (cysteine and methionine) and thus, biomagnifies through food webs. Other organic Hg-complexes are dimethylmercury, phenylmercuric acetate, and methylmercury chloride.

- **Particulate Hg (Hg_p).** Consists of Hg bound in, or adsorbed on, particulate matter and is generally not very bioavailable.

The different chemical forms and oxidation states of Hg can cycle indefinitely between atmospheric, aquatic and terrestrial environments. There are two main physico-chemical processes important for bioavailability of Hg in biota: oxidation-reduction and methylation-demethylation processes.

Oxidation-Reduction processes

In order to enter the biosphere and the food web, the relatively unreactive Hg^0 must be oxidized to a more reactive form (Hg^{2+}). The oxidation of Hg^0 to Hg^{2+} in the atmosphere has been thought to have ozone (O_3) as the primary oxidant (Munthe, 1992; Iverfeldt and Lindqvist, 1986), but it was recently shown that the reaction is an unlikely pathway for atmospheric conditions (Calvert and Lindberg, 2005). It is still unclear which oxidant dominates, but bromine (Br) is known to cause rapid loss of Hg^0 in the Arctic boundary layer in spring (Schroeder et al., 1998; AMAP, 2002). Oxidation of Hg^0 is thought to be controlled by photochemistry, thus production of Hg^{2+} is thought to peak during midday (Selin, 2009).

Since Hg^{2+} has low volatility and reactive properties, when Hg^0 is converted to Hg^{2+}, it can be rapidly taken up in rain water, snow or adsorbed onto small particles, and subsequently be deposited in the environment via wet or dry deposition. Once oxidized, 60% of atmospheric Hg is deposited to land and 40% to water, even though land only represents 30% of the Earth’s surface (Morel et al., 1998). The dry-deposition on land will vary depending on the effective surface areas from different types of vegetation, and whether it is forested or non-forested areas. Additionally, part of the dry-deposited Hg will be retained in the canopy (sorption on plant surface or uptake by stomata) and the rest will be washed-off by precipitation and end up as throughfall water (Iverfeldt, 1991).

Methylation-Demethylation processes

The concentrations of MeHg are the net result of the biotic and abiotic processes producing and degrading MeHg, i.e., the methylation and demethylation processes. Methylation of inorganic Hg to MeHg and demethylation of MeHg are two fundamental processes determining the levels of MeHg in the aquatic ecosystems.

In aquatic environments, methylation is primary microbial, inorganic Hg is converted to MeHg by sulfate- and iron-reducing bacteria (Benoit et al., 2001; Kerin et al., 2006). Methanogens have also been demonstrated to be primary methylators in lakes (Hamelin et al., 2011). The methylation processes can follow both biotic and abiotic pathways in both terrestrial and aquatic ecosystems. In lakes, the methylation mainly occurs in bottom sediments, but can also take place in water. Methylation processes are affected by a variety of environmental factors such as, nutrient availability, water temperature, organic material, sulfur cycling, salinity, pH or redox conditions (Ullrich et al., 2001). Methylation is generally favored by acidic and anaerobic conditions, with moderately high temperatures and high concentrations of organic matter (Ullrich et al., 2001).

An abiotic methylation is also possible if suitable methyl donors are present (Ullrich et al., 2001). The process depends on environmental factors including pH, temperature or the presence of complexing agents such as chloride. Some of the methylating agents include small organic molecules such as methylcobalamin, methyltin and methyl iodide (Celo et al., 2006).

The decomposition of MeHg in aquatic environments is also performed by bacteria and has two different pathways: reductive and oxidative demethylation (Barkay and Wagner-Doebler, 2005). MeHg is reduced to volatile elemental Hg (Hg^0) and methane (CH_4), while the oxidative demethylation results in the production of divalent Hg (Hg^{2+}), CO_2 and CH_4 (Lehnherr, 2014). Both pathways are performed by different groups of microorganisms. Abiotic processes also include photolytic decomposition of MeHg (photodemethylation) by solar radiation in lake surface waters (Sellers et al., 1996; Mason and Benoit, 2003; Lehnherr and St Louis, 2009).

1.3 Distribution of mercury in ecosystems

Fluxes of both natural and anthropogenic Hg derive from point and diffuse sources, and subsequent emissions from land, freshwater and oceans. When Hg cycles between the atmosphere, water, sediment and soil, it undergoes a series of complex chemical, physical, and biological transformations, many of which are still not completely understood.

Hg enters the atmosphere as a gas (Hg^0) making up for 95% of the THg, or bound to airborne particles (Hg_p). It can then be deposited in the environment by either wet- or dry-deposition. In aquatic ecosystems, the ultimate source of Hg is deposition from the atmosphere, usually associated with rainfall or snow. Once in the water, Hg enters a complex cycle of reactions between the different chemical forms. It can also be settled in the sediments, enter the food web and/or be released back to the atmosphere by volatilization (Fig. 1).

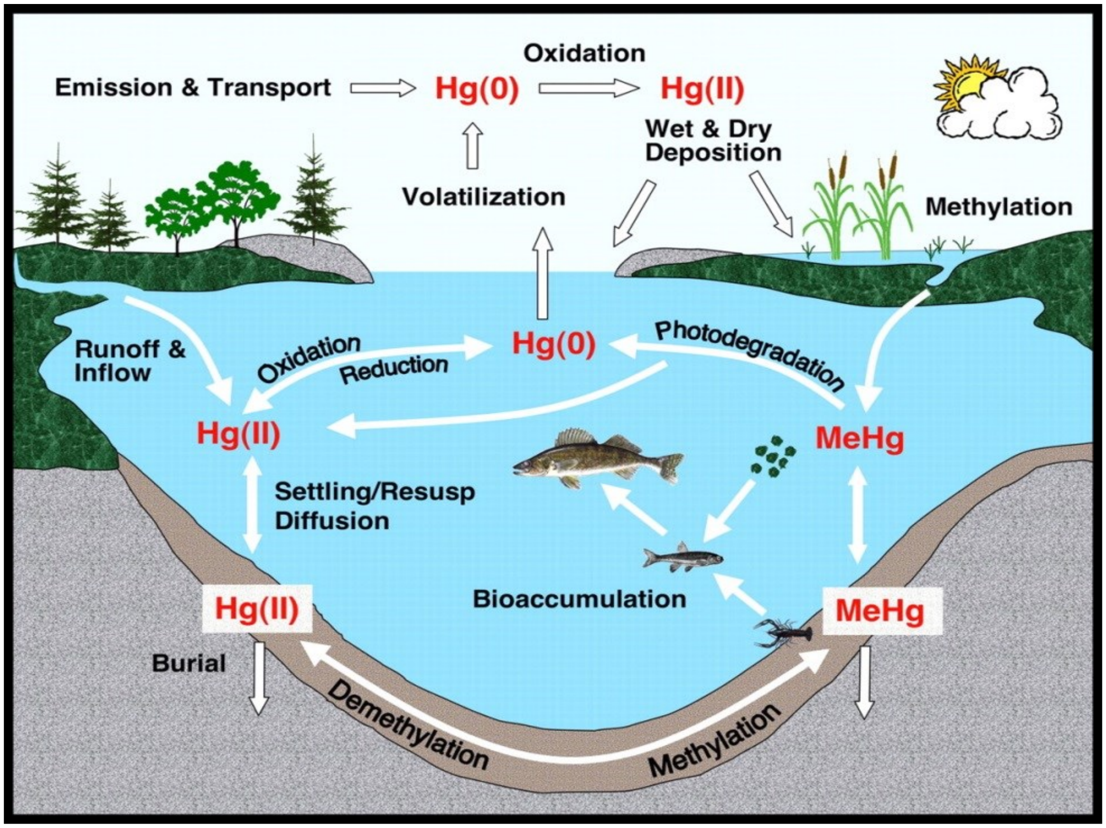


***Fig. 1** Hg cycle in aquatic ecosystem (*Source: *Engstrom, 2007).*

The Hg load into lakes includes direct inputs to the lake surface, indirect inputs from terrestrial catchment discharge, and internal processes within the lake (Fig. 1). MeHg is the most important chemical form of Hg regarding accumulation and biological effects on biota, thus the interactions between total Hg load, the microbial transformation of Hg, the water chemistry (redox potential, E_h, pH, temperature, dissolved organic carbon, etc.) and the food web structure, are essential factors for the MeHg concentration in lake water and, subsequently, in lake biota (Ullrich et al., 2001; Boszke et al., 2002; Engstrom, 2007; Arctic Pollution, 2011; Liu et al., 2012). Thus, as the Hg concentration in aquatic biota is highly dependent of the amount of MeHg, a THg concentration seldom explains the Hg levels in aquatic biota. This may explain why an increase in Hg concentrations in fish may occur, despite a total reduction in THg input, as it has been reported in several Norwegian lakes (Fjeld and Rognerud, 2009).

Watershed landscapes, especially wetlands, constitute an important source of MeHg to downstream aquatic ecosystems. In watersheds from northern latitudes, wetlands are often an important terrestrial landscape component. Wetlands play an important role in the Hg cycle and represent “hot spots” for bacterial Hg methylation (Grigal et al., 2000; Hall et al., 2008; Branfireun et al., 1998; St. Louis et al., 1994). The percentage of wetland areas in lake catchments is positively correlated to the MeHg levels in downstream waters, suggesting that wetlands export MeHg to lakes and rivers (Rudd, 1995; Hurley et al., 1995). This could probably explain why fish in brown-water lakes, which receive a significant inflow from wetlands, often have high concentrations of MeHg (Driscoll et al., 1994).

1.4 Stable isotopes of carbon and nitrogen

Stable isotope analysis (SIA) of nitrogen (^{14}N and ^{15}N) and carbon (^{12}C and ^{13}C) is an important technique for characterizing food web structure and understanding the pathways of energy flow through the food web (Peterson and Fry, 1987; Kling et al., 1992; Cabana and Rasmussen, 1996).

Despite the minor mass difference between isotopic forms of an element, isotopes function slightly different in various physical, chemical and biological processes. Generally, the lightest isotope (^{12}C or ^{14}N) tends to form weaker bonds and react faster than the heavier isotopes (^{13}C or ^{15}N). As a consequence, the abundance of stable isotopes of an element will vary between chemical species. Isotope fractionation is the change in isotopic abundance between chemical species due to physical or chemical processes (Gannes et al., 1998).

The stable isotope composition is usually expressed as a ratio of heavy to light isotope (δ values) relative to an internationally accepted reference standard. The use of ratios allows for large variations (in per mil, ‰) to be observed between samples that slightly differ in the percentage composition of given isotopes. Therefore, the isotopic composition is expressed as follows:

$$\delta X = \left(\frac{R_{sample}}{R_{standard}} - 1\right) * 1000$$

where X is the heavier isotope, and R is the corresponding ratio between the heavy and light isotope, $^{13}C/^{12}C$ or $^{15}N/^{14}N$, in the sample and the standard. Increases in δ values denote increases in the amount of the heavy isotope components. Conversely, decreases in δ values denote decreases in the heavy isotope content, and a reciprocal increase in the light isotope component (Peterson and Fry, 1987). Isotope ratios are measured using mass spectrometry, which separates the different isotopes of an element on the basis of their mass-to-charge ratio.

Two natural stable C isotopes exist: ^{12}C (98.89 %) and ^{13}C (1.11 %), with a natural ratio $^{13}C/^{12}C$ (δ ^{13}C) of 0.112 ‰ (1.11/98.89). The reference standard material is C in the PeeDee limestone. This standard consists of a calcium carbonate from a Cretaceous belemnite from the Peedee Formation in South Carolina (Craig, 1953). The nomenclature has been changed to VPDB, Vienna-Pee-Dee-Belemnite (Coplen, 1994).

Two natural stable N isotopes exist: ^{14}N (99.64 %) and ^{15}N (0.36 %), with a natural ratio $^{15}N/^{14}N$ ($\delta^{15}N$) of 3.61 ‰ (0.36/99.64). The isotope ratio in a sample is compared to the standard N ratio in the air (Mariotti, 1983).

Carbon and nitrogen fractionation

It has been shown that an animal's diet is isotopically reflected in its tissues. Consumers become enriched in ^{15}N relative to their diet by 3.4 ‰ per trophic level (Minagawa and Wada, 1984; Post, 2002). In contrast, the isotope fractionation of C through the food web is relatively conserved in each trophic level transfer, only about 0.4 ‰ (Post, 2002). Several stable C isotope data from different sources are shown in Table 3.

Table 3 *$\delta^{13}C$ signatures from different carbon sources (France, 1995b; O'Leary, 1988; Rognerud, 2003)*

Material	**$\delta^{13}C$ (‰)**
VPDB $\delta^{13}C$ standard	0
Atmospheric CO_2	-8
C3 plants	-29 to -25
C4 plants	-16 to -12
CAM plants	-20 to -10
Freshwater macrophytes	-16 ± 4
Small plankton algae	-36 to -30
Periphyton	-22 to -18
Turf, humus	-27 ± 3

When analyzing an animal's diet, the most common method has usually been the analysis of stomach contents, feces or food remains. However, gut content only gives a picture of the last meal at a specific time (a snapshot analysis), but might not reflect the overall diet. Thus, stable isotopes of N and C in animals' tissues integrate dietary components over a much longer period of time (Hesslein et al., 1993) and they provide an average estimate of an organism's preferred diet (DeNiro and Epstein, 1978; Pinnegar and Polunin, 1999).

In aquatic ecosystems, $\delta^{13}C$ is useful for differentiating between two major sources of available energy: pelagic and littoral. Pelagic consumers mainly base their food sources on autochthonous primary productivity, like phytoplankton, while littoral consumers are mainly sustained by attached algae and detritus (France, 1995b). The $\delta^{13}C$ signature of the littoral food web tends to be enriched in ^{13}C (less negative $\delta^{13}C$) compared to the signature of the pelagic food web (France, 1995b) (Fig. 2). Benthic algae tend to be ^{13}C enriched compared to phytoplankton, as a consequence of the greater water turbulence to which planktonic algae are exposed, which reduces the boundary layer thickness and may cause ^{13}C depletion (France, 1995b). The $\delta^{13}C$ signature is generally lighter (^{13}C depleted) in plants by increasing water depth, because of increased incorporation of respired CO_2, which is more abundant in deeper water of stratified lakes (Rognerud et al., 2003).

There are primarily three energy sources in aquatic ecosystems: plankton algae C, periphyton C and terrestrial C (Fig. 2).

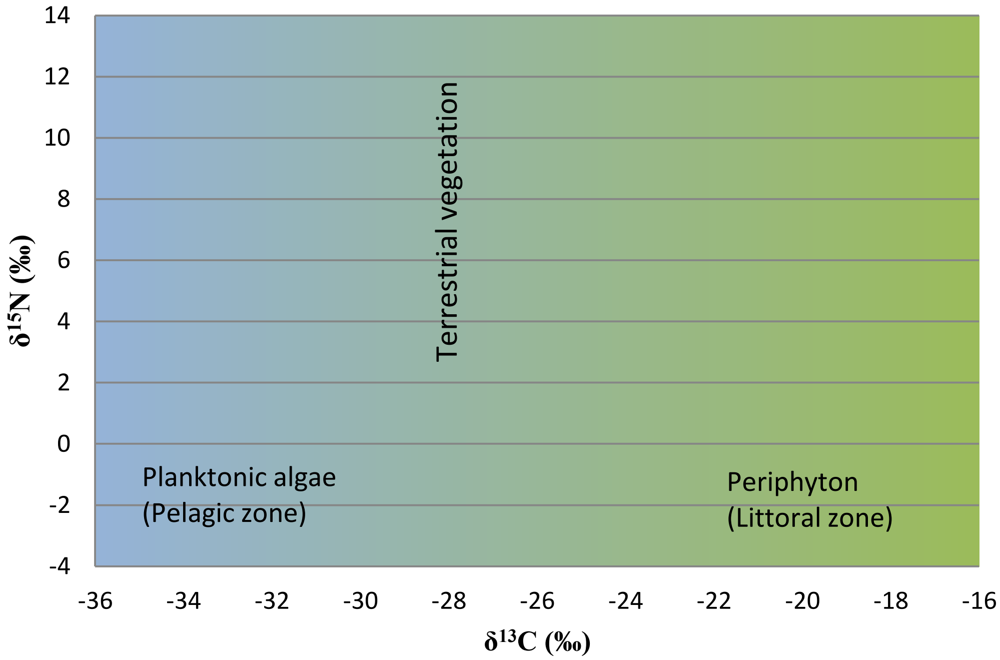


Fig. 2 *Principal energy sources in aquatic ecosystems.*

Enrichment of $\delta^{15}N$ occurs at successive levels allowing for estimates of relative trophic position within a food web (Cabana and Rasmussen, 1996; Vander Zanden and Rasmussen, 1999). The enrichment of N from prey to predator could be explained by two mechanisms: isotope fractionation favoring the heavy N (^{15}N) during protein synthesis from amino acids, as most of the body N is in the form of protein; or isotope fractionation favoring the light N (^{14}N) in the process of N elimination (Schoeller, 1999).

In general, the $\delta^{15}N$ signatures become heavier as the $\delta^{13}C$ signatures become lighter. This is caused by a change in N sources for primary producers as the importance of other C sources changes (Rognerud et al., 2008).

However, to obtain the high level of resolution required to discern complex trophic interactions, stable isotopes should be used together with other information, such as direct diet analyses from stomach content (Post, 2002).

Baseline corrections

When comparing food webs from different lake ecosystems, the $\delta^{15}N$ and $\delta^{13}C$ values of an organism alone provide little information about its absolute trophic position or ultimate source of C (Post, 2002). Therefore, an appropriate isotopic baseline correction is needed (Cabana and Rasmussen, 1996). This is likely due to considerable variations between ecosystems at the base of the food web from which organisms draw their N and C (Post, 2002).

Variations in primary producers or primary consumers also exist within a system, to the extent that the signature of one primary consumer may not reflect that of any other primary consumer in the same system. It is due to habitat-specific differences in baseline $\delta^{13}C$ and $\delta^{15}N$. According to DeNiro and Epstein (1981), different individuals of a same species raised with the same diet can have significantly different $\delta^{15}N$ values. Vander Zanden and Rasmussen (1999) studied the spatial variability in stable isotopic values of primary consumers as a function of feeding habitat (Table 4). Therefore, different basal sources should be taken into consideration when baseline correcting the isotopic signatures of different fish individuals from an ecosystem, due to the behavior of fish feeding across different habitats.

Table 4 *Mean values of $\delta^{13}C$ and $\delta^{15}N$ from primary consumers sampled in 14 lakes in Canada (Vander Zanden and Rasmussen, 1999).*

	Littoral	**Pelagic**	**Profundal**
$\delta^{13}C$	-23.8 ‰	-28.4 ‰	-30.5 ‰
$\delta^{15}N$	1.6 ‰	3.1 ‰	5.2 ‰

The $\delta^{15}N$ values may reveal temporal fluctuations due to seasonal variations in N source input to lakes. Accordingly, gastropods or bivalves are suitable organisms for bottom line corrections because gastropods feed on periphyton and bacteria, the lowest trophic level in the benthic food webs, and bivalves feed on seston (algae and bacteria), the lowest trophic level of the pelagic food web. Both groups live relatively long and therefore reduce seasonal fluctuations typical from short-lived organisms. Thus, both are suitable for baseline corrections for benthic and pelagic food webs, respectively (Post, 2002).

In oligotrophic clear water lakes, benthic invertebrates are important prey for many fish species. In such case the periphyton-feeding gastropod *Lymnaea peregra* has commonly been used in Norwegian lakes. The baseline corrections are made by the following equation (Rognerud et al., 2003; Post, 2002):

1) $\delta^{15}\text{N-k}$ (‰) = $\delta^{15}\text{N}_{\text{fish}}$ (‰) – $\delta^{15}\text{N}_{L.\ peregra}$ (‰)

2) $\delta^{13}\text{C-k}$ (‰) = $\delta^{13}\text{C}_{\text{fish}}$ (‰) – [$\delta^{15}\text{N-k}$ (‰) / 3.4] $*$ 0.4

Thus, the interpretation of isotopic signatures of higher trophic level consumers, after being baseline corrected by long-lived primary consumers such as snails and mussels, will provide a measure of food chain length related to bottom-up mass transfer that can then be compared between lakes (Cabana and Rasmussen,1996). Vander Zander et al. (1997) confirmed the ability of baseline adjusted δ^{15}N signatures to represent the trophic position of aquatic consumers. However, obtaining an appropriate baseline is a difficult methodological issue regarding the effective application of stable isotopes to describe trophic food webs (Post, 2002).

Stable isotope fractionation in fish

Fish have a key role in aquatic food webs, they are important consumers from diverse sources, and may occupy multiple trophic levels, often being on the top of the aquatic food web (Vander Zanden and Vadeboncoeur, 2002). Therefore, they are widely used in the evaluation and understanding of trophic interactions in aquatic food webs.

When analyzing individual tissues of a single fish, differential fractionations might occur. Frequently, dorsal white muscle, bone collagen or fish liver are sampled. The whole fish is analyzed when it is too small for any individual tissue to be sampled (Pinnegar and Polunin, 1999). According to Pinnegar and Polunin (1999), white muscle is less variable in δ^{13}C and δ^{15}N than all other tissues, and it is probably the best tissue for use in ecological work.

Lipid synthesis discriminates against ^{13}C in favor of the lighter isotope (^{12}C), thus, tissues that contain large amounts of lipids tend to be more depleted in ^{13}C compared with whole organisms (Pinnegar and Polunin, 1999). The extraction of lipid prior to stable isotope analysis can produce significantly different δ^{13}C values for freshwater and marine fishes and invertebrates

(Søreide et al., 2006). Elsdon et al. (2010) demonstrated that extracting lipids from fish muscle increased both $\delta^{13}C$ and $\delta^{15}N$ by approximately 1‰.

Starving animals exhibit elevated $\delta^{15}N$ enrichment (Hobson et al., 1993), presumably because animals catabolize their own body proteins, producing isotopic enrichment analogous to that of ingested food (Gannes et al., 1998).

Trophic levels in aquatic organisms

A correct description of the trophic relationships in an ecosystem is of critical importance for many ecological studies, especially for studies focusing on the bioaccumulation of contaminants, such as Hg, in top predators. A broad definition for "trophic level" of an organism is the position that it occupies in a food chain, although the assumption of a single linear chain is very simplified (Polis and Strong, 1996). Because N isotope ratios become enriched at successive trophic levels, it is possible to estimate an individual trophic position. However, obtaining the isotopic baseline required to estimate a trophic position for an organism is one of the most difficult problems (Post et al., 2000b). The simplest formula for calculating the trophic position of an organism is:

$$3)\ \text{Trophic position} = \lambda + (\delta^{15}N_{\text{organism}} - \delta\ ^{15}N_{\text{base of the food web}})/3.4$$

where λ is the trophic position of the organism used to estimate $\delta\ ^{15}N_{\text{base of the food web}}$ (being $\lambda=1$ for primary producers and $\lambda=2$ for primary consumers), $\delta^{15}N_{\text{organism}}$ is the direct isotopic measure and 3.4 is the average enrichment of $\delta^{15}N$ per trophic level (Post, 2002).

However, organisms acquire N from more than one food web. As mentioned previously, fish feed on both littoral and pelagic food webs and obtain their $\delta^{13}C$ signatures from two major sources with distinct isotopic signatures, and it is possible to determine the fraction of littoral and pelagic energy contribution (Karlsson and Byström, 2005). Therefore, consumer organisms also acquire their $\delta^{15}N$ signatures from more than one food web (Post et al., 2000b; Vander Zanden and Vadeboncoeur, 2002) and the simplest formula for calculating the trophic position (eq. 4) can be reformulated to a more accurate two-source food web model:

$$4)\ \text{Trophic position} = \lambda + (\delta^{15}N_{\text{organism}} - [\delta\ ^{15}N_{\text{pelagic}}\cdot\alpha + \delta\ ^{15}N_{\text{littoral}}\cdot(1-\alpha)])/3.4$$

where α is the proportion of C in an organism that is derived from the base of the pelagic food web: $\alpha = (\delta^{13}C_{fish} - \delta^{13}C_{littoral})/(\delta^{13}C_{pelagic} - \delta^{13}C_{littoral})$.

Aquatic food web dynamics

The early approaches to trophic structures were very simple linear food chains with discrete levels such as "plant-herbivore-predator", in which the species at lower trophic levels tend to be more abundant than those at higher trophic levels (Elton, 1927). This classic food chain concept has been replaced by a more realistic concept: the food web. Food webs are a complex network of interactions among species within an ecosystem, and can be strongly influenced by the behavior and movement of predators, energy and nutrients across boundaries (Post et al., 2000a). An example of a simplified freshwater food chain and a food web in a lake are outlined in Fig. 3.

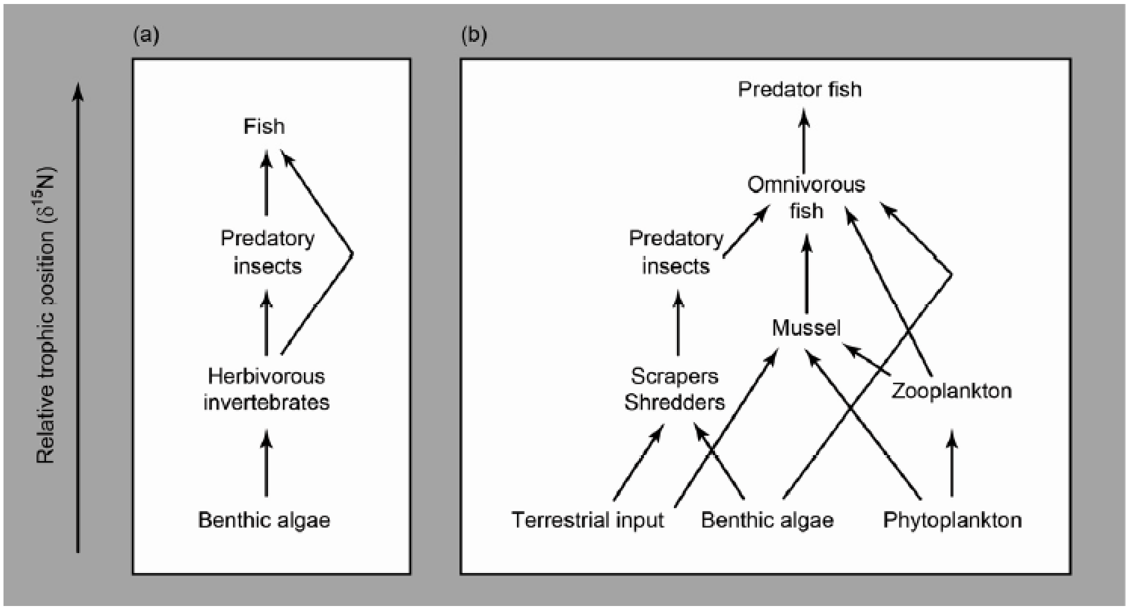


Fig. 3 *Simplified food webs in a lake. (a) Simple littoral food chain with four trophic levels. (b) Food web in which primary production and allochthonous matter are both potential energy inputs. (Source: Soto et al., 2013).*

The classic food chain theory considered the pelagic food webs in lakes as simple food chains based on phytoplankton production, and were often modeled as simple linear food chains with either three or four trophic levels (Hairston and Hairston, 1993). This view has been questioned by the recognition of multi-chain omnivory (Vander Zanden and Vadeboncoeur, 2002; Karlsson and Säwström, 2009). It has been documented that omnivory is more the rule than the exception because most consumer species feed at different sources in natural freshwater systems (Soto Arrojo, 2011).

Vander Zanden and Vadeboncoeur (2002) concluded that the duality of pelagic and benthic production pathways in lakes, linked by mobile consumers such as fish, is an important pattern for the understanding of food web dynamics in lakes. Therefore, it is considered that fish derive energy opportunistically from both habitats (Post et al., 2000a).

The ecological importance of terrestrial organic matter to lake food webs has become an important subject. It is of special importance in boreal humic lakes where much of the organic matter is derived from the catchments (allochthonous production) and where autochthonous production is limited due to the restriction of light penetration (Meili et al., 1996; Grey et al., 2001). However, autochthonous organic matter is also crucial for the growth of higher consumers in lakes and cannot be fully replaced by allochthonous resources (Karlsson et al., 2012) (Fig. 3b).

It has been demonstrated that terrestrial organic matter constitutes an important source of C and energy for pelagic organisms (Carpenter et al., 2005; Karlsson et al., 2012). The isotopic composition of zooplankton has been shown to have a significant contribution from both allochthonous and autochthonous C sources (Karlsson et al., 2003). Thus, zooplankton should not be considered as a single trophic functional group, since each species of zooplankton behaves differently and assimilates C in different proportions from littoral or pelagic sources (Grey et al., 2001).

In summary, two complex trophic concepts, such as the incorporation of omnivory and the allochthonous inputs, are essential for the understanding of the dynamics of aquatic food webs (Soto Arrojo, 2011).

1.5 Mercury in aquatic biota

Hg remains a significant global problem and a human health issue. Bioaccumulation of Hg in fish has been more intensively studied than in other aquatic organisms, probably due to fish being a primary source of food and the dominant route of exposure to MeHg for both humans and piscivorous wildlife. Although in the water phase MeHg represents only 3–5 % (interquartile range) of the THg in boreal lakes in South-East Norway (Braaten et al., 2013), more than 95 % is in the methylated form in fish muscle tissue and directly obtained from the diet (Bloom, 1992; Huckabee et al., 1979). MeHg is effectively and readily taken up by biota and it biomagnifies through the food web, from microorganisms like plankton, benthic invertebrates, to small fish, piscivorous fish, fish-eating birds and mammals, including humans. In lakes, the relative bioaccumulation depends on the lake chemistry and processes which govern the speciation of Hg^{2+} and MeHg (Mason et al., 1995).

MeHg has the tendency to bind to sulfhydryl groups (-SH) associated to protein and amino acids such as cysteine (Harris et al., 2003), which plays an important role in the transport of Hg in the body. It is likely the reason why the highest MeHg concentrations are found in muscle tissues, although it alone cannot account for it. Other tissues such as liver, kidney or spleen are also shown to accumulate Hg (Giblin and Massaro, 1973), however, they contain a lower percentage of MeHg than muscle tissue likely due to the higher proportion of fat. Muscle is the most often sampled tissue due to its higher content in proteins, but also because it is the most commonly consumed part of the fish.

MeHg biomagnifies in food webs due to its excretion being much slower (3-fold) than that for Hg^{2+} and its assimilation efficiency being 5 to 10-fold higher. In addition, excretion rates are slower in larger animals and at colder water temperatures (Trudel and Rasmussen, 1997). Bioconcentration factors in the order of 10^4 to 10^7 have been reported in the step between water and algae/seston (Ullrich et el., 2001; Stein et al., 1996; Watras et al., 1998). However, the transfer of MeHg from the aquatic environment to the biota at the base of the food web is still not well understood, but it is mediated by methanogens and sulfate- and iron-reducing bacteria (Benoit et al., 2001; Kerin et al., 2006; Hamelin et al., 2011).

Ecosystems with high methylation rates of inorganic Hg^{2+} generally have fish with elevated concentrations of Hg as it greatly increases the Hg availability for incorporation into the food web (Wiener et al., 2003). The accumulation of Hg in an organism is affected by bioavailability and by the organism's bioenergetics (Kidd et al., 2011). Different factors in fish biology affect the Hg bioaccumulation rates, such as species, size, age or diet. Generally, Hg concentrations in fish increase with increasing age and body size (length and weight), which is likely the result of a slow rate of MeHg elimination relative to the fast rate of uptake (Bodalay et al., 1993; Trudel and Rasmussen, 1997; Gilmour and Riedel, 2000). Hg concentration in fish also increases with trophic position, estimated using stable isotopes of N (McIntyre and Beauchamp, 2007; Garcia and Carignan, 2005; Cabana et al., 1994; Vander Zanden and Rasmussen, 1996). This shows the importance of understanding the food web structures and bioenergetics in aquatic ecosystems.

Fish growth rate has been shown to modulate Hg concentrations (Simoneau et al., 2005). Rapid growth rates are hypothesized to decrease the mass-specific MeHg concentration in fish and other aquatic organisms by a process called somatic growth dilution (SGD). The process of biodilution occurs when the growth rate of the fish exceeds the bioaccumulation rates, leading to reduced mass-specific Hg concentrations (Stafford et al., 2004; Karimi et al., 2007; Sharma et al., 2008). In other words, fish with low activity costs are expected to contain lower levels of Hg in their muscle tissue (Trudel and Rasmussen, 2006). Conversely, the opposite process occurs during the winter period, with slow fish growth and higher Hg concentrations. During this starvation period fish catabolize their own muscle tissue to use as energy, reducing the body mass faster than the bound MeHg, with the subsequent increase of the overall Hg concentration in the fish muscle (Cizdziel et al., 2002). Presumably, these two processes, growth dilution and starvation-concentration, are the main explanation for the seasonal variations of Hg in many lakes.

Fish size is a factor that can easily vary among sampling periods, therefore seasonal changes in Hg concentrations in aquatic ecosystems have been investigated in many studies aiming to describe seasonal patterns in freshwater food webs (Farkas et al., 2003; Gorski et al., 1999; Meili and Wills, 1985; Murphy et al., 2007; Park and Curtis, 1997; Slotton et al., 1995; Staveland et al., 1993; Ward and Neumann, 1999; Zhang et al., 2012). However, some studies record no seasonal changes in Hg concentrations in fish muscle tissue (Burger et al., 2009; Farkas et al., 2000; Foster et al., 2000). Consequently, since Hg concentrations in specific fish tissue may vary over time, the relative influence of factors such as environmental fluctuations (pH, temperature, dissolved organic carbon, nutrient availability) and changes in fish physiology should be taken into account when investigating Hg concentrations in fish (MassDEP, 2006).

Even though Hg emissions have declined in the past decades (Pacyna et al., 2006; Wängberg et al., 2007), recent reports from Scandinavia (Åkerblom and Johanson, 2008; Fjeld and Rognerud, 2009) showed an unexpected increase of the Hg content in fish. Several explanations have been suggested, such as climate change, with warmer and wetter climate, longer growing seasons, or forestry practices. Hongve et al. (2012) suggested that the substantial decrease of acid rain pollution in Norway during the last decades has enhanced the Hg concentrations in fish. One of the effects of reduced acid rain is increased dissolved organic carbon (DOC) in runoff to lake waters (Monteith et al., 2007). This will lead to enhanced Hg transport from the catchments to surface waters and, in combination with the increase in DOC, increased in-lake Hg methylation may occur, subsequently causing elevated Hg concentrations in fish (Hongve et al., 2012).

In addition, concentrations of Hg in one fish species can vary considerably from lake to lake due to among-system differences in water chemistry, and watershed characteristics (Chen et al., 2005). Hg concentrations also vary within and among regions. Limnological variables such as lake pH (Brown et al., 2010), DOC concentration (Driscoll et al., 1995), water color (Nilsson and Håkanson, 1992), nutrient availability (Foe and Louie, 2014), and alkalinity (Spry and Wiener, 1991) have been shown to correlate with fish Hg concentrations. Hg levels in fish have been shown in experimental studies to respond directly and rapidly to a change in the Hg inputs from atmospheric deposition (Harris et al., 2007).

Based on the guideline levels established by Codex Alimentarius Comission (Joint FAO/WHO food standard programme) in 1991, the European consumption limit for Hg in fish muscle tissue is 0.5 mg Hg/kg (0.5 ppm), except for certain larger predatory species (pike) having a consumption limit of 1.0 mg Hg/kg (1 ppm).

1.6 Wildfires and aquatic ecosystems

Forest disturbances, and especially forest fires, strongly influence the Hg cycle. Forest fires are a major source of Hg as the accumulated Hg in the forests is released to the atmosphere. Emissions from forest fires have been shown to correspond to high percentages of the anthropogenic emissions (Wiedinmyer and Friedli, 2007). Hg is not only present in the forest soils but also on the forest canopy, accumulating in the foliage due to a high adsorption surface. It concentrates in the most vulnerable parts for combustion during a fire such as leaves and needles, small branches, bark, mosses and lichens, and, predominantly organic soil (Wiedinmyer and Friedly, 2007; Turetsky et al., 2006; Friedly et al., 2007).

The type of catchment plays an important role, since for example Hg stocks are greater in boreal peatland soils than in forested soils (Turetsky et al., 2006). In the watersheds, the Hg associates with the organic matter, so perturbations such as fires or clear-cut logging, may alter Hg export rates to lakes and influence in-lake processes.

Forest ecosystems contain high amounts of nutrients and Hg equivalent to many years of deposition. Forest fires cause the release of elemental Hg (Hg^0) to the atmosphere, by the process of volatilization, from soils as well as from living and dead vegetation (Navrátil, 2009). Wildfires alter the soil and vegetation within the burned area affecting nutrient transport (Miesel et al., 2012) which may produce a nutrient pulse in lakes, stimulate the bacterial production, and therefore, influence the formation and availability of MeHg to the biota.

The results from a study by Kelly et al. (2006) demonstrated that forest fires can cause increased Hg accumulation in the biota from partially burned catchments. The reasons for such conclusions were food web restructuration due to enhanced productivity and increased Hg inputs and MeHg production. On the other hand, Garcia and Carignan (2000) did not document any significant fire effects on the Hg accumulation in fish, while Allen et al. (2005) documented a decrease in fish Hg concentrations attributing it to increased inputs of nutrients with a subsequent increase of lake productivity.

The water quality of the lakes within a wildfire area may also be directly affected. The combustion remains which are left in the wildfire area are rich in base cations, phosphate, chlorides, heavy metals (Eriksson et al., 2003; Kelly et al., 2006) and pyrolytic polycyclic aromatic hydrocarbons (Finkelstein et al., 2005). With the increase of runoff after fire (Schindler et al., 1980; Bayley et al., 1992b) there is an enhanced wash-off of materials into streams and lakes. Many studies have documented increases in major base cations, strong acid anions, ammonia, total N and total P in surface water from many wildfire studies (Schindler et al., 1980; Lamontagne et al., 2000; Carignan et al., 2000; Bayley et al., 1992a,b; Eriksson et al., 2003). It has also been reported a decrease in pH and acid neutralizing capacity (Bayley et al., 1992b; Eriksson et al., 2003).

Stable isotope fractionation also occurs during forest fires since all biogeochemical processes undergo some degree of kinetic isotope fractionation. The $\delta^{15}N$ and $\delta^{13}C$ signatures in the aquatic biota from wildfire affected watersheds have been shown to be influenced by wildfires. Silins et al. (2014) reported an enrichment in both $\delta^{15}N$ and $\delta^{13}C$ signatures of macroinvertebrates in a Canadian lake; while Spencer et al. (2003) found $\delta^{15}N$ enrichment but $\delta^{13}C$ depletion in both macroinvertebrates and fish, reporting clear evidence that wildfires can significantly influence the energy pathways of aquatic food webs. It has been suggested that a shift from allochthonous to autochthonous energy sources might explain these enrichments, as France (1995c) reported that autochthonous food sources had more enriched $\delta^{15}N$ signatures than terrestrial allochthonous sources. On the other hand, the high overlap in $\delta^{13}C$ signatures between allochthonous and autochthonous matter makes it more difficult to assess dietary shifts in consumer organisms (France, 1997).

2. OBJECTIVES

The overall purpose of the thesis was to investigate the Hg levels in fish muscle tissue from different aquatic ecosystems in southern Norway, in both natural and wildfire impacted lakes. The main objectives of this thesis can be summarized as:

- The description of a food web from a relatively big southern Norwegian lake, focusing on feeding habitats and trophic positions (by use of carbon and nitrogen stable isotopes, $\delta^{13}C$ and $\delta^{15}N$) for different fish species, as well as the Hg fluctuations due to variations in parameters such as age, length, weight, habitat use or trophic levels (*Paper I*).

- The determination of seasonal variations in the Hg concentrations in fish muscle from three different species in a lake in southern Norway, with focus on finding the stronger explanatory factors for such fluctuations (*Paper II*).

- The investigation of the effects of a wildfire on aquatic ecosystems, focusing on Hg levels in the freshwater and throughout the food chain. Differences between years of post-fire Hg concentrations in perch are assessed. Variations of major chemical compounds in lakes from the wildfire affected catchment area are studied during a period of four years (*Paper III and IV*).

3. RESULTS AND DISCUSSION

There are a number of factors known to influence the Hg concentrations in fish muscle tissue. The results from this investigation provide an overview of the Hg levels in fish from two relatively large lakes in Telemark county (papers I and II) and in nine smaller lakes in Mykland, a wildfire impacted area (paper III), in southern Norway. Many physical and chemical characteristics of the aquatic ecosystem (paper IV) as well as biological factors may influence the fish Hg concentrations. These factors may mislead the interpretation of the results if not taken into account and may point to erroneous conclusions.

The results showed that the highest Hg concentrations were found in piscivore species such as northern pike (*Esox lucius*, 2.50 ppm ww) or large brown trout (*Salmo trutta*, 1.95 ppm ww), while the lowest Hg concentrations were found in a small crucian carp (*Carassius carassius*, 0.028 ppm ww) and a whitefish (*Coregonus lavaretus*, 0.040 ppm ww). Older and larger piscivorous fish species tend to accumulate more Hg as they age, likely as a result of the slow rate of MeHg excretion relative to the fast rate of uptake (Bodaly et al., 1993; Trudel and Rasmussen, 1997; Gilmour and Riedel, 2000). Differences of almost two orders of magnitude (0.028 – 2.50 mg Hg kg^{-1}) were observed in the Hg concentrations in the investigated fish, therefore showing the importance of controlling for confounding factors such as age, fish size and trophic position when interpreting Hg concentrations, in order to avoid incorrect conclusions. In our studies, we used statistical analysis of covariance to control for the potential effects on Hg of length, body mass, age or $\delta^{15}N$ signatures of the fish.

Trophic dynamics including community structure and feeding habits ($\delta^{15}N$ and $\delta^{13}C$) or environmental factors (watershed disturbance or seasonal fluctuations) play important roles in the bioaccumulation of Hg in aquatic ecosystems and are discussed next.

3.1 Seasonal fluctuations of Hg concentration in fish

The main source of Hg in fish is their diet. As a result, seasonal changes in diet composition can have an important influence on the fish Hg concentrations. Additionally, Hg levels are influenced by fish size (Gilmour and Riedel, 2000), a factor that can readily fluctuate between sampling periods. Our data confirmed seasonal variations in fish Hg concentrations from Lake Heddalsvatn accounting for confounding factors such as fish length or age (paper II: Table 3), but the causes may vary depending on fish species.

The cold and dark environment during winter periods in boreal areas, normally with ice covered lakes, implies minor biological production at all ecosystem levels. Thus, many fish show a decline in the feeding activity during winter (Greenfield et al., 2005) and a degree of starvation likely appears. On the other hand, during the fish growth season the feeding activity, growth rate and growth efficiency are at their highest (Lindqvist et al., 1991) and therefore, the body mass increases rapidly (Talbot, 1993). Due to these processes, seasonal variations are expected in fish Hg concentrations and $\delta^{15}N$ signatures.

Generally, the highest Hg concentrations in fish muscle tissue (adjusted for covariates) of pike and whitefish were observed during the winter time in Lake Heddalsvatn (paper II). One of the main biological mechanisms described to influence fish Hg concentrations is somatic growth dilution (Verta, 1990; Ward et al., 2010; Lepak et al., 2012). Fast growing fish assimilate more biomass relative to the incorporation of Hg than slow grower fish, thus diluting the Hg by the extra body mass. The perch individuals showed an increase in mass throughout the summer (from May to September) with a subsequent decrease of Hg concentration in muscle tissue, being somatic growth dilution the most likely explanation, as also shown in other investigations (Stafford et al., 2004; Meili, 1991). The seasonal changes of Hg in pike could not be explained by growth dilution, since there was no measurable growth from May to September. An explanation might be the single capture site within a restricted area of the lake, which may have biased the results. The whitefish individuals had very low Hg concentrations in all three seasons, likely explained by the feeding habits on benthos and zooplankton. Despite so, seasonal variations were found, but as the sampled individuals did not show measurable growth from May to September, it cannot be explained by growth dilution.

3.2 Hg biomagnification in aquatic food webs ($\delta^{15}N$)

The trophic magnification slope (TMS), i.e. the slope of the simple linear regression between $\log_{10}$-transformed Hg and measured-$\delta^{15}N$ in biota, is often used as a measure of the biomagnifying potential of Hg in the aquatic food web and was calculated for all investigated lakes in this thesis. Additionally, the trophic magnification factor (TMF = $10^{3.4*TMS}$) represents the increase of Hg concentration per trophic level. A recent report by Lavoie et al. (2013) throughout different regions and ecosystems worldwide, showed TMS mean values of temperate freshwater lakes of 0.16 ± 0.10 (n = 65) for THg and 0.24 ± 0.07 (n = 78) for MeHg. Our result for THg from Lake Norsjø (paper I) was almost identical to the TMS by Lavoie et al. (2013), while the TMS values from the other study lakes were slightly higher (Table 5). The higher TMS values based on THg in the smaller lakes were comparable to the TMS values for MeHg by Lavoie et al. (2013). This agrees well with the fact that more than 95% of the Hg in fish muscle is in the methylated form (Bloom, 1992; Huckabee et al., 1979). In addition, many biogeochemical factors in the lakes and watersheds might explain differences in Hg and TMS between lakes. Different TMS values between food webs are most likely regulated by the Hg availability at the base of the food web (Stewart et al., 2008). Thus, the intercept value of the regression might be an important factor. The higher intercept values were found in Lake Hundsvatn and Lake Øyvatn, indicating higher Hg levels at the bottom of the food web, and the fact that that the highest intercepts occurred 2 years after the fire (paper III: table 4), might indicate a wildfire effect.

Table 5 *Trophic magnification slopes (TMS ± standard deviation), trophic magnification factor (TMF), intercept, coefficient of determination (r^2) and p-values based on wet weight THg concentration for the lakes included in this investigation.*

LAKE	***TMS***	***TMF***	***Intercept***	***r^2***	***p***
Norsjø	0.16 ± 0.017	3.58	-2.45	0.45	0.000
Heddalsvatn	0.19 ± 0.018	4.29	-2.25	0.28	0.000
Hundsvatn*	0.22 ± 0.014	5.60	-1.96	0.83	0.000
Øyvatn*	0.22 ± 0.013	5.60	-1.89	0.81	0.000
Melestjenn*	0.25 ± 0.020	7.08	-2.24	0.78	0.000

* Including fish and invertebrates.

Also, other ecosystem characteristics and processes within the food web might influence the TMS values (Borgå et al., 2012) and thus potential explanatory factors for the various TMS values found in our lakes (paper III). Lavoie et al. (2013) showed that both THg and MeHg concentrations in biota were positively correlated to latitude, with higher bioaccumulation potential in polar sites than tropical sites. Different physico-chemical factors may explain these trends, such as processes related to temperature, DOC concentrations or pH. These factors are discussed below.

The regressions between $\log_{10}$Hg and δ^{15}N in biota are also strongly influenced by the number of trophic levels included in the samples. Thus Borgå et al. (2012) recommended at least 3 trophic levels to be included in such estimates. Assuming a δ^{15}N enrichment of 3.4 ‰ per trophic level (Minagawa and Wada, 1984; Post, 2002), fish individuals caught in Lake Norsjø covered 2.5 trophic levels and fish from Lake Heddalsvatn covered 2.4 trophic levels, while Lake Hundsvatn, Lake Øyvatn and Lake Melestjenn covered 3.0, 2.6 and 2.7 trophic levels, respectively.

In northern latitudes, such as boreal and sub-arctic areas, peatlands occupy 15% of the region and contain approximately one third of the world's soil C pool, which in turn supply most of the DOC entering boreal lakes (Gorham, 1991; Bridgham et al., 2001; Pastor et al., 2003; Wieder et al., 2006). Lavoie et al. (2013) found a positive relationship between TMS values and DOC. Our results follow a similar trend as Lake Melestjenn had the highest TMS and TOC concentration, compared to Lake Norsjø with the lowest TMS and TOC concentration. However, contradictory results regarding DOC and Hg concentrations have been found in other studies (Rolfhus et al., 2011; Dittman and Driscoll, 2009).

It is well established that Hg has a strong affinity for organic matter and in freshwaters more than 90% of Hg has been estimated to be complexed by organic matter (Meili, 1997). DOC influences production, transport and uptake of MeHg by different processes, which in sum might result in both positive and negative effects on Hg in biota (Watras et al., 1995). On the one hand, DOC competitively binds Hg species relative to particles at elevated DOC concentrations and it also strongly binds Hg^{2+} and/or $MeHg^{+}$ immobilizing Hg for biological uptake (Gerbig et al., 2011). On the other hand, DOC has also been shown as a mechanism for increased solubilization from particles, leading to the possible increase in bioavailability of inorganic Hg for methylating organisms (Hall et al., 2008). DOC as an organic C source, stimulates microbial activity, including Hg-methylators, and decreases the photo-demethylation rates (Wiener et al., 2006). Thus, DOC plays a complex role in the biogeochemistry of Hg and it is therefore a complex predictor of Hg levels in aquatic organisms.

Variations in lake water pH can also explain variations in TMS values, even though Lavoie et al. (2013) could not find a relationship, likely due to an incomplete data set. However, a link between high Hg concentrations in fish and lake acidification has been observed before (Grieb et al., 1990; Wiener et al., 1990, 2006). Kelly et al. (2003) suggest that lake acidification should be considered as one of the contributing factors to high fish Hg concentrations in soft water lakes. Several mechanisms can explain the negative relation between Hg levels in fish and lake pH. There are higher methylation rates (Xun et al., 1987) and greater Hg^{2+} uptake by the methylating bacteria at lower pH (Kelly et al., 2003). Lower pH also reduced the amounts of negatively charged sites with direct effects on DOC-Hg interactions, making Hg^{2+} more available to bacteria and in turn, increasing methylation rates (Miskimmin et al., 1992). Also, a higher dominance of Hg-methylating microorganisms at lower pH might be another factor (Winch et al., 2008). Our results do not show a clear trend between lake pH and TMS values, but a multiple lake study in south-eastern Norway by Fjeld and Rognerud (2009), in relatively acidic lakes (pH: 5.2 – 6.5) with high TOC content (5 – 15 mg C L^{-1}) exhibited very similar TMS values (median TMS = 0.22) to that observed in our small, boreal lakes in the wildfire area in southern Norway (paper III).

Water temperature is another important factor for Hg biomagnification in aquatic systems (Lavoie et al., 2013). At lower temperatures, as in high latitude regions, fish growth rates are slower (Handeland et al., 2008) leading to slower elimination rates of MeHg (Trudel and Rasmussen, 1997), therefore increasing the Hg biomagnification potential. Additionally, Lavoie et al. (2013) hypothesized that the simpler food webs and low species diversity in high latitude regions (Hillebrand, 2004) might lead to increased Hg bioaccumulation due to lower prey diversity for a given consumer, potentially increasing the efficiency of Hg transfer along the food web.

3.3 Stable isotope analyses

Stable isotope fractionation does occur in more or less degree in all biogeochemical processes. In our studies, assimilation of inorganic C in primary producers, energy assimilation along the food web, starvation (paper II) and watershed disturbances such as wildfires (paper III), are all isotope fractionation processes.

In paper II we have studied seasonal variations in $\delta^{15}N$ and Hg in order to reveal potential growth dilution (Verta, 1990; Ward et al., 2010; Lepak et al., 2012) or starvation effects (Cizdziel et al., 2002) on these variables. The $\delta^{15}N$ signatures from fish sampled in May and December were significantly higher compared with September. These seasonal variations in the $\delta^{15}N$ signatures in fish from our study were associated with fluctuations in mean body size. Moreover, after adjusting for length as covariate, the $\delta^{15}N$ signatures for pike and whitefish were not significantly different between seasons, while for perch there was a small significant decrease ($\Delta^{15}N = -0.7‰$) from May to September. Thus, our seasonal $\delta^{15}N$ fluctuations are likely not an effect of starvation, although starvation is known to produce higher $\delta^{15}N$ in fish (Macko et al., 1986; Gannes et al., 1998). The main reason for this is the deamination and transamination (internal rearrangement of N) occurring during starvation, which means excretion of lighter N (more ^{14}N enriched) with subsequent more enriched ^{15}N left in the animal's body (Macko et al., 1986; Gannes et al., 1998). Accordingly this increase in $\delta^{15}N$ does not reflect any increase in trophic level.

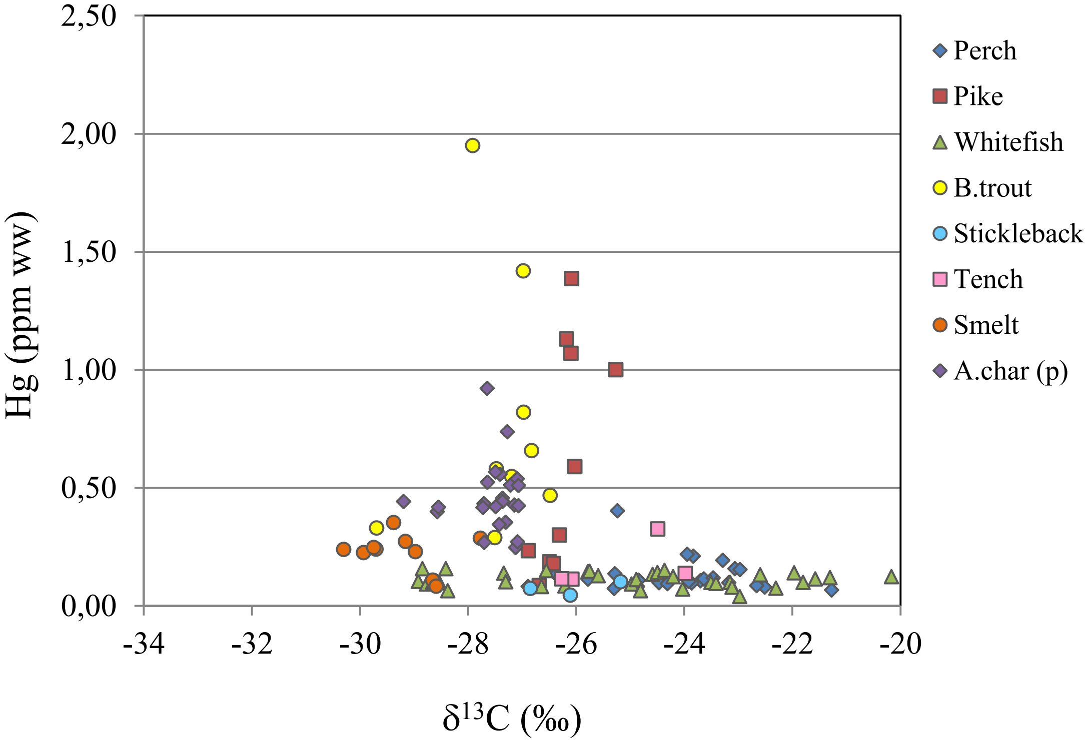
In paper III we have studied potential effects of wildfire on stable isotopes and Hg in biota. The two wildfire affected lakes, Lake Hundsvatn and Lake Øyvatn, had higher $\delta^{15}N$ signatures in fish two years after the wildfire, adjusted for length and age covariates. Enrichment in $\delta^{15}N$ signatures from aquatic organisms during post-fire periods has been documented and described earlier. Silins et al. (2014) proposed that the higher $\delta^{15}N$ values could be linked to shifts in the ingested food items following the fire, a shift from allochthonous to more autochthonous energy sources at the macroinvertebrate level. Spencer et al. (2003) also speculated that a shift in the diet could explain this enrichment, or an increase in the assimilation of fine particulate organic matter. During a wildfire fractionation occurs in the soil inorganic N as pyrolysis causes a progressively more ^{15}N-enriched soil while ^{14}N is preferentially lost by volatilization. Because of these pyrolysis and/or volatilization processes happening in the soils during fires, Stephan (2007) argued that attributing more enriched $\delta^{15}N$ signatures in aquatic organisms to a change in their food sources, from terrestrial to aquatic, is not totally correct, due to the changes that the terrestrial food's $\delta^{15}N$ signatures undergo during a fire. However, we might not exclude natural year-to-year variations as potential explanatory factors as well. The variations in the thermocline depths during the years might influence the redox potential, which in turn have direct effects on the ammonification and denitrification processes near the oxycline and deeper in the hypolimnion, with direct effects on inorganic δ^{15}N signatures in water and soil (Wada and Hattori, 1978; Macko et al., 1986) and thereby also on the δ^{15}N signatures in biota.

Saito et al. (2007) suggested that these fire-induced changes may be useful for tracing the fire effects on water quality and for monitoring the recovery of the aquatic ecosystems. However, stable isotope signatures may only be used as tracers if the fire impacts are larger than the already natural variability existing in the food webs.

3.4 Horizontal food web structure (δ^{13}C, energy source) and Hg in fish

As mentioned before, almost all Hg in fish is directly derived from their diet. As the various primary-producer habitats do isotope fractionation of inorganic C in various degrees, and a minimal organic C fractionation up the food web, δ^{13}C measurements might be a useful tool to distinguish between different organic C sources (terrestrial, littoral, pelagic, profundal) in different food webs. The δ^{13}C signatures do not reflect the direct food consumption of aquatic organisms as fish, but give a time-integrated view of the individual's diet.

Large variations occurred in the relationship between δ^{13}C and Hg in fish from our investigated lakes. In Lake Norsjø (paper I), the piscivore species (brown trout, pike and Arctic char) with the highest Hg concentrations exhibited the most intermediate δ^{13}C signatures among all the studied species (Fig. 4). This means that their diets are supported by a mix of both pelagic and benthic resources, which in turn indicates that they strongly integrate across littoral and pelagic food chains and habitats. The remaining fish species showed lower Hg concentrations and while European smelt (most pelagic) and three-spined stickleback (most littoral) clustered at the outer edges of the pelagic-littoral gradient, whitefish had individuals from obligate benthic to obligate zooplanktonic diet. Similar to Lake Norsjø, the piscivorous pike and the opportunistic perch from Lake Heddalsvatn (paper II) exhibited the most intermediate δ^{13}C signatures and the highest Hg concentrations, while whitefish showed the largest range in δ^{13}C signatures. In the much smaller lakes from the wildfire affected area (paper III), with only perch and brown trout present, the δ^{13}C signatures reflected a predominant littoral-derived diet, but as the terrestrial δ^{13}C signatures are very similar to the littoral signatures, it is impossible to distinguish between benthic- and terrestrial-derived organic C in these food webs.



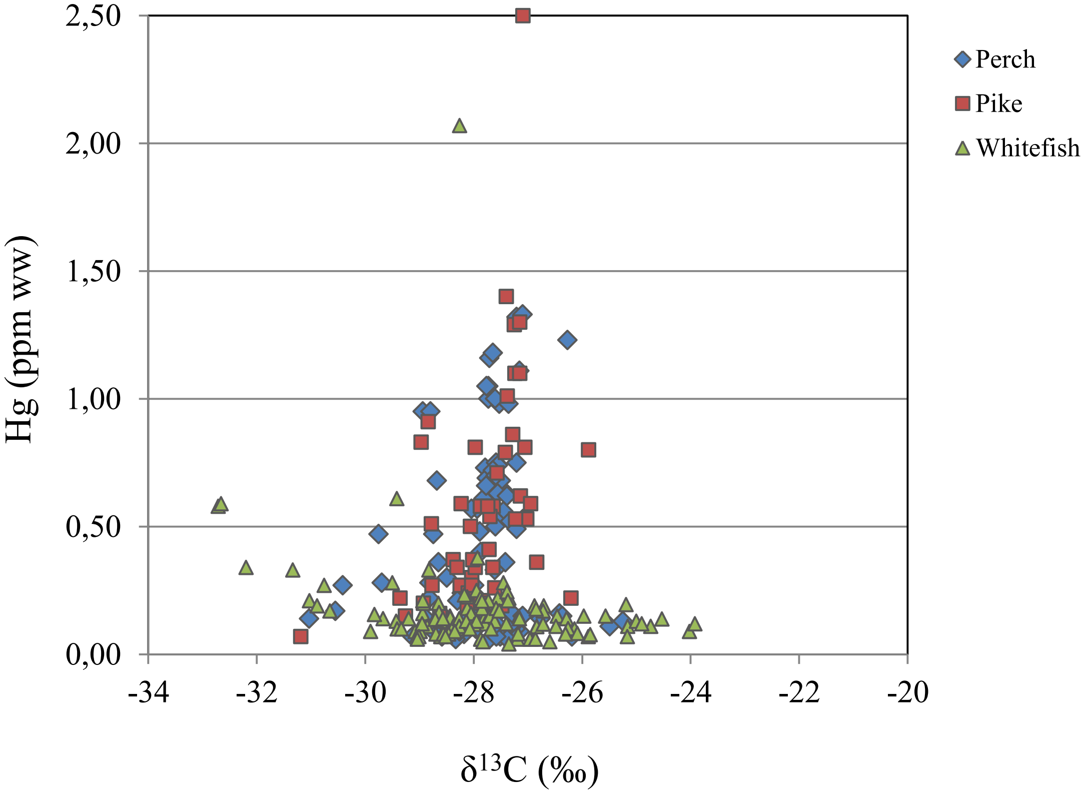


Fig. 4 *Measured* $\delta^{13}C$ *(‰) versus Hg concentrations (ppm ww) in several fish species from Lake Norsjø (top) and Lake Heddalsvatn (bottom).*

Fish are mobile species usually integrating various food webs, thereby deriving their energy opportunistically from several habitats, primarily from littoral and pelagic habitats (Post et al., 2000a; Vander Zanden and Vadeboncoeur, 2002). However, their main limitation for habitat use will always be a balance between food availability and predator avoidance.

Lindqvist et al. (1991) stated that both vertical (relative trophic position, $\delta^{15}N$) and horizontal (energy source, $\delta^{13}C$) food web structures are crucial factors for the Hg concentrations in fish. It has been hypothesized that fish feeding on pelagic-derived C sources often have high Hg concentrations (Gorski et al., 2003; Power et al., 2002). The study by Power et al. (2002) in a small shallow oligotrophic lake indicated that the fish Hg concentrations varied systematically with the C sources, showing an increase of Hg as the contribution from pelagic-derived C increased. Gorski et al. (2003) compared two similar small lakes and found that the lake with more pelagic-based food web exhibited higher Hg concentrations in large adult fish individuals. However, in Lake Norsjø and Lake Heddalsvatn, bigger and much deeper lakes, the highest Hg concentrations were found in piscivore species with intermediate $\delta^{13}C$ signatures, i.e. species supported by a mixed diet of littoral and pelagic food webs.

However, one should be careful about doing inter-lake comparisons of $\delta^{13}C$ and Hg levels in aquatic biota, as there are overlaps in $\delta^{13}C$ signatures between various organic C sources (France, 1997). This means that $\delta^{13}C$ analyses should be supported by stomach analyses of prey animals, and the fact that the amount of C derived from pelagic and littoral sources is very dependent on lake size (Vander Zanden and Vadeboncoeur, 2002). Assuming littoral and pelagic-derived C as the main energy sources in lakes, a simple two-source mixing model can estimate the contributions of the two sources in the diet of fish individuals (Vander Zanden and Vadeboncoeur, 2002). In paper I, we have applied such a model for Lake Norsjø, only based on stable isotope analyses in fish. By this model we can indirectly quantify the percentage contribution of food derived from littoral and pelagic habitats, termed the indirect zoobenthos reliance, for each species or at individual levels. The individual approach is probably the most realistic approach, as individuals within each fish species may prefer different habitats and/or diets, due to factors as ontogeny, or they might simply have different foraging behaviors, which may imply large variations in $\delta^{15}N$ and $\delta^{13}C$ within each fish species. Values of $\delta^{13}C$ in zoobenthos and zooplankton were used as end-members in this model, and based on the measured $\delta^{13}C$ in individual fish, the zoobenthos/zooplankton ratio was estimated for each fish individual. These individual ratios were further used for individual baseline correction of $\delta^{15}N$. By this model, the highest indirect zoobenthos reliance was found in perch (89 ± 14%) while the lowest was found in smelt (37 ± 7%). Among piscivore species, pike had the highest estimated zoobenthos reliance (65 ± 6%), followed by Arctic char (54 ± 5%) and brown trout (53 ± 11%).This model indicated that there was a generally high zoobenthos reliance across most species in Lake Norsjø, a relationship that was somewhat unexpected as it is a large and deep lake (55.48 km^2, mean depth: 87m). Vander Zanden and Vadeboncoeur (2002) clearly demonstrated the strong negative correlation between zoobenthivory and lake area. Despite the significant importance of pelagic communities to the overall ecosystem production in large lakes (Tilzer, 1990), substantial amounts of littoral-derived C are still produced and assimilated in local food webs, such as in the deep (0-20 m) Årnes Bay from Lake Norsjø. In the small lakes in the Mykland area, the fish $\delta^{13}C$ signatures (-31.8 ‰ to -25.8 ‰) were very similar to those in the zoobenthos (-31.2 ‰ to -25.6 ‰) in all the study lakes, including wildfire impacted and reference lakes (paper III, figure 2). This is a strong evidence of predominant littoral-derived food webs in these lakes, and concurs well with the negative relationship between zoobenthos reliance and lake size described by Vander Zanden and Vadeboncoeur (2002).

Additionally, the relatively depleted $\delta^{13}C$ values presented in fish from the Mykland area, compared with periphytes-predominant littoral C lakes, indicates that allochthonous C might be an important C source in small, TOC rich boreal lakes. Moreover, in TOC rich systems with significant decomposition of organic C the respired CO_2 produced is depleted in ^{13}C (Rau, 1978, 1980). This suggests that littoral produced C might be more $\delta^{13}C$ depleted (due to algal uptake of respired CO_2) in lakes with high TOC content than clear-water lakes, thus exhibiting a $\delta^{13}C$ signature closer to terrestrial C sources. The overlap in C isotope ratios from terrestrial vegetation and littoral-derived organic C, makes it difficult to differentiate between aquatic (autochthonous) and watershed (allochthonous) food dependency (France, 1997). As many natural factors for variations in $\delta^{13}C$ exist, it is very difficult to distinguish effects of wildfire from natural variations.

3.5 Effects of wildfire on aquatic ecosystems

The part of this study that focuses on Mykland, the wildfire impacted area, demonstrates that watershed disturbances, such as wildfires, can produce biological and physico-chemical responses in the lakes and aquatic communities (papers III and IV).

Mykland is located in an area with slowly weatherable rocks and thin soil cover, has been heavily burdened by long-range air pollution transport for decades, and lakes and rivers have been strongly acidified, primarily by sulphuric acid (Høgberget, 2010). Therefore, the lakes are typically characterized by low pH, low ionic strength, low acid neutralizing capacity (ANC) and low concentrations of nutrients (Tot-P < 6-7 μg L^{-1}, NO_3^- < 40 μg L^{-1}, NH_4^+ < 5 μg L^{-1}), and moderately impacted by allochthonous organic C (TOC: 4-6 mg C L^{-1}).

The most extreme water chemical effects (paper IV) were documented during a strong rain event two months after the fire, in August 2008, when the soil water was again fully replenished, and significant runoff occurred. During the first post-fire rain events, strong acid anions (Cl^- and SO_4^{2-}) were mobilized faster from terrestrial to aquatic systems in comparison with base cations, thereby decreasing the ANC. For a lake with low pre-fire ANC values, as Lake Hundsvatn, a significant drop in ANC might occur (-80 μeq L^{-1}) and, accordingly, an increase in H^+ and in toxic inorganic aluminium (Al_i), potentially harmful to aquatic biota (Al_i = 326 μg L^{-1}). Conversely, for a lake with higher pre-fire ANC values as Lake Øyvatn, the drop in ANC was smaller and harmless to aquatic biota. During the first post-fire year, the ANC values seem to be reestablished (paper IV: figures 3 and 4).

There was a certain increase of nutrients (N and P) during the first extreme rain events; however, the concentrations were still relatively low, likely due to the fact that boreal forests are nutrient poor environments, particularly in N (Foster and Morrison, 1976; Gosz, 1981). There was a post-fire periodical increase in N-compounds during winter and snowmelt episodes, as documented in other studies (Carignan et al., 2000; Mast and Clow, 2008). In addition, the N-uptake by vegetation has increased and, thus N-concentrations are close to background concentrations during growth season. As there are no comparable pre-fire tot-P measurements, we cannot quantify the immediate effects of the wildfire.

The decrease of TOC during the first post-fire year was followed by a gradual increase during the next years. Similar post-fire trends have been documented in other studies (McEachern et al., 2000; Carignan et al., 2000). The initial decrease might be related to the combustion of organic matter during the fire, while the subsequent increase in TOC the following years might be due to the new vegetation being re-established in the area.

Chl-*a* levels increased during the first post-fire growth season, and gradually decreased during the next 4 years to close to pre-fire concentrations (paper III, figure 1). The high concentrations in lake Melestjenn during summer was caused by algae (80-90% of the volume was *Botryococcus braunii* and *Gonyostomum semen*) which are likely not important for consumers or even toxic (Rengefors et al., 2012; Chiang et al., 2004).

In paper III, a water analysis survey was implemented in June 2012, four years after the wildfire, including analysis of THg and MeHg. The watershed characteristics are some of the most important factors that regulate the concentration and availability of THg and MeHg (Driscoll et al., 1995) and the lakes included in our study present very different characteristics (Paper IV: table 3). All lakes are relatively small (0.0091 – 0.89 km^2) and shallow (2.5 – 15 m deep), but with relatively large variations in draining ratio (CA:LA from 1.4 to 335) and lake residence time (0.023 – 3.2 years).

The concentrations of THg and MeHg ranged from 1.17 - 2.63 ng L^{-1} and from 0.053 - 0.188 ng L^{-1}, respectively (Paper III: table 3). A strong positive correlation between THg and MeHg with TOC was found, concurring with others (Driscoll et al., 1995, Eklöf et al., 2012, Braaten et al., 2014), as DOC is the main transport vector of Hg through the watershed (Grigal, 2002) and more than 90% of Hg is estimated to be complexed by organic matter (Meili, 1997). The three reference lakes had the highest concentrations of TOC; two of them, Lake Svarttjenn and Lake Melestjenn are the lakes with the highest THg, MeHg and %MeHg (Paper III, table 3?). In addition, THg and MeHg concentrations were also strongly and positively correlated with variables demonstrated to correlate with TOC, such as color and Tot-P (Meili, 1992).

Lake Svarttjenn and Lake Melestjenn (reference lakes) are the two smallest lakes from our study, with the strongest color values and the highest TOC and MeHg concentrations. In addition, TOC was negatively correlated with lake size, as documented in other studies (Braaten et al., 2014; Watras et al., 1995). Bodaly et al. (1993) suggested the size of a lake to be a determining factor for Hg concentrations due to small lakes typically being warmer than larger lakes, and usually having higher rates of methylation in relation to demethylation. At the same time, most colored lakes are small, shallow lakes with large catchment areas (Rasmussen et al., 1989). Lake Svarttjenn was the lake with the biggest catchment area, the largest wetland area and the smallest lake-to-catchment area ratio compared to the other lakes in the study. These factors likely affected the high concentrations of THg and MeHg found in the lake.

Methylation is a primary microbial process by sulphate reducing bacteria (SRB) and iron reducing bacteria (IRB) and thus, factors affecting this process play an important role. A strong negative correlation between SO_4^{2-} and TOC was found in our lakes and has also been documented before in streams and lakes (Evans et al., 2005; Borg and Sundbom, 2014). Since organic matter is a substrate for SRB, an increase in TOC can lead to higher bacterial activity and thus, a lower SO_4^{2-}concentration in lake water. Also, two reasons might explain the strong positive correlation found between Tot-Fe and MeHg. First, higher concentration of Fe may lead to higher methylations rates by IRB and thus, higher MeHg. Second, iron hydroxides play an important role in the aquatic Hg cycle due to their large surface area and capacity to adsorb Hg and release it after their dissolution under lower redox conditions (Ramalhosa et al., 2006; Ullrich et al., 2001).

Forest wildfires alter the soil and vegetation, consequently affecting the nutrient transport to lakes (Miesel et al., 2012) and the amount of organic C storage (McEachern et al., 2000; Carignan et al., 2000). As the DOC transport from terrestrial to aquatic systems was initially reduced after the wildfire (paper IV), the immediate effect would imply decreased Hg input to lakes. However, as TOC in the wildfire affected lakes increased gradually after the first post-fire year, a gradual increase of Hg to lakes should also be expected, as DOC is the main vector of Hg transport through the watersheds (Grigal, 2002). Therefore, perch was used to reveal potential year differences (2008, 2010 and 2012) of Hg in biota, including two wildfire impacted lakes: Lake Hundsvatn and Lake Øyvatn; and a reference lake: Lake Melestjenn (paper III).

The highest Hg concentrations in perch, adjusted for covariates, occurred in 2010, two years after the fire, but only statistically significant for Lake Øyvatn, not for Lake Hundsvatn. There was a decline in the adjusted Hg concentrations in 2012 compared with 2010, in both Lake Melestjenn and Lake Øyvatn. The fact that we do not have data for the reference lake during

2008 means that the high Hg concentrations found in 2010 cannot be directly considered an effect of the fire.

In 2010 there was a deeper thermocline and bigger volume of epilimnion compared to 2012. Small boreal lakes in this latitude are not permanent dimictic lakes and year-to-year variations occur; some years lake stratification might occur before the hypolimnion is fully oxygenated, thus affecting the redox conditions. Hg methylation is highest in anoxic waters (Ullrich et al., 2001) therefore, having a deeper thermocline (and oxycline) might likely affect the Hg content in fish.

Moreover, as fires can increase the input of nutrients to lakes (Spencer et al., 2003), a subsequent increase in algal productivity might occur. Algal bloom dilution is a main biological mechanism (together with somatic growth dilution) that influences fish Hg concentrations. When algal biomass in a lake increases, the Hg is distributed among a larger biomass, in turn decreasing the Hg concentration per unit of mass, and thus causing a lower dietary intake of Hg (Pickhardt et al., 2002). However, the highest fish Hg concentrations found in 2010 coincide with the highest levels of tot-P and chl-*a*, thereby not reflecting this Hg dilution theory. On the other hand, higher chl-*a* might also suggest enhanced algal production and increased availability of labile organic matter, which in turn can stimulate microbial activity and the methylation processes (Foe and Louie, 2014). Furthermore, MeHg concentrations in algae are higher in DOC rich waters (Pickhardt et al., 2006). A positive correlation was found between aquatic MeHg and chl-*a* in the surface water of our lakes in 2012; this is an interesting observation as phytoplankton is the main Hg entry point to the food web and has the highest biomagnification factor (water phase to phytoplankton), thus Hg burden at this stage of the food web is crucial.

Additionally, the higher THg concentrations found in the zooplankton from the wildfire impacted lakes (0.27 ± 0.03 ppm dw) than in the reference lakes (0.20 ± 0.07 ppm dw), four years after the fire, cannot be directly considered as an effect of the fire as these measurements were conducted four years after the fire, and the water chemical conditions were close to pre-fire levels (paper IV).

The differences in years described for fish Hg concentrations coincide with the adjusted $\delta^{15}N$ levels in fish, i.e. highest in all lakes in 2010. As this was also the case in the reference lakes, year-to-year variations might be a key factor.

Overall, several physico-chemical and biological factors might have impacted the Hg concentrations in fish during our study, making it difficult to draw strong conclusions regarding wildfire effects on fish Hg concentrations.

4. CONCLUSIONS

Several factors are observed to affect the Hg concentrations in fish from our study. Analysis conducted to evaluate the variation in Hg concentrations regarding feeding habitats, seasonal fluctuations and potential wildfire effects in fish from fire impacted lakes showed that the Hg concentrations varied widely, both within and between fish species and study sites. The application of stable isotope analysis was used to estimate the relative contribution of food derived from littoral or pelagic habitats and to estimate the relative trophic position.

A two-source (littoral and pelagic) mixing model at individual level in fish from Lake Norsjø confirmed that most species had generally high zoobenthos contribution in their diets. A baseline correction in the stable isotope signatures is implemented as fish species with distinct feeding modes can overlap or present large variations in $\delta^{13}C$ and $\delta^{15}N$. The individuals with more intermediate $\delta^{13}C$ signatures were the piscivore species (northern pike, brown trout and Arctic char) indicating that their diets are supported by both littoral and benthic C sources. This was a pattern also observed in Lake Heddalsvatn. Moreover, these species integrating across littoral and pelagic food chains and habitats had the highest Hg concentrations.

Seasonal variations are documented in the Hg concentrations in fish. Generally higher Hg concentrations were found during winter time and during the month of May, disregarding confounding factors such as age or length. The interplay between low feeding rates during winter (starvation) and somatic growth dilution during the summer is the main reason explaining the fluctuations of Hg concentrations in fish in high latitude lakes. However, this was only true for perch as the sampled pike and whitefish individuals did not show measurable growth throughout the summer time.

Trophic magnification slopes (TMS) were used to assess the potential biomagnification of Hg through the food web and were highest in small boreal TOC-rich lakes. The biomagnification slopes concurred with other studies and the values were affected by ecosystem characteristics and factors such as TOC levels, pH or temperature-related processes. The highest intercept values (estimates of Hg concentrations incorporated at the base of the food web) were observed in the small boreal lakes, with even higher levels two years after the wildfire occurred, indicating possible wildfire effects.

The wildfire occurred in an area characterized by thin topsoil and high precipitation rates. These thin organic soils are readily exposed to rain and fire and are prone to be washed out. Consequently, the most severe post-fire effects were observed during the initial hydrological post-fire episodes. During these events faster mobilization of anions as chloride and sulfate compared with base cations caused significant ANC decreases in the lakes. At the same time, a certain increase in nutrient (N and P) runoff was documented and a decrease of TOC due to combustion of organic matter during the fire. Main water chemistry was almost re-established one year after the wildfire and almost all parameters seem to be back to pre-fire conditions 4.5 years after the wildfire. Besides the hydrological regime affecting the water chemistry, the catchment topography, lake morphometry (catchment-to-lake area ratios and residence times), geology, fire intensity or fraction of burnt catchment are also decisive factors for water chemistry variations both in time and space.

From our analyses, an increase in the Hg concentrations from perch caught two years after the wildfire was apparent. The observed increased levels of nutrients and chl-*a* might be key factors to explain this Hg increment. However, natural year-to-year variations of physico-chemical factors as the thermocline and the redox status of a lake are important factors that might influence the Hg concentrations in biota and makes it difficult to draw strong conclusions on wildfire effects.

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Papers I-IV

Paper II

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Seasonal variation of mercury and δ^{15}N in fish from Lake Heddalsvatn, southern Norway

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ABSTRACT

Seasonal variations of mercury (Hg) concentration in muscle tissue of northern pike - *Esox lucius* L, European whitefish - *Coregonus lavaretus* L and European perch - *Perca fluviatilis* L have been investigated in Lake Heddalsvatn, southern Norway. Our data confirmed seasonal differences in the Hg concentrations in fish, but the causes for that may vary depending on fish species. Length (pike and perch) and age (perch and whitefish) were the strongest explanatory factors for the Hg fluctuations. Fish caught in December (pike and whitefish) had the highest Hg concentrations, while the concentrations in May were higher than in September for all 3 species, statistically significant for perch ($P<0.0001$) and close to significant for pike ($P=0.07$). Higher δ^{15}N signatures were found in December and May compared with September, but these differences might be related to fish body size variations. There was a large range of δ^{13}C signatures in the investigated fish, but no significant differences between seasons neither within nor between species.

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INTRODUCTION

Mercury (Hg) is naturally present in waters at very low concentrations. The more toxic form of Hg, the monomethylmercury, CH_3Hg^+ (MeHg), is a toxicant readily accumulated by aquatic biota. Although in the water phase MeHg only represents 3–5 % (interquartile range) of the total Hg in boreal lakes in South-East Norway (Braaten *et al.*, 2014), more than 95 % is in the methylated form in muscle tissue and directly obtained from the diet (Huckabee *et al.*, 1979; Bloom, 1992). Therefore, the methylation of inorganic Hg is a crucial process regulating mercury levels in fish (Korthals and Winfrey, 1987). Microbial Hg transformations play an important role in the Hg cycle, the production of MeHg occurs primarily through methylation of inorganic Hg by sulfate-reducing bacteria (Benoit *et al.*, 2001) and iron-reducing bacteria (Kerin *et al.*, 2006).

In addition to the methylation rates, there exist a number of other environmental, ecological and physiological factors influencing the bioaccumulation of Hg in aquatic ecosystems (Watras *et al.*, 1998; Ullrich *et al.*, 2001). These factors may mislead the interpretation of the results of many studies, leading to erroneous conclusions and hiding other possible relationships (MassDEP, 2006). Therefore, while apparent Hg concentrations in specific fish tissue may vary over time, the relative influence of factors such as environmental fluctuations (pH, temperature, dissolved organic carbon, nutrient availability) and changes in fish physiology should be taken into account when results are interpreted (MassDEP, 2006). Concentrations of Hg can be influenced by fish size (Gilmour and Riedel, 2000), a factor that can easily vary among sampling periods. Hence, seasonal changes in the Hg concentrations in aquatic ecosystems have been investigated and documented in many studies aiming to describe seasonal patterns in freshwater food webs (Meili and Wills, 1985; Staveland *et al.*, 1993; Slotton *et al.*, 1995; Park and Curtis, 1997; Gorski *et al.*, 1999; Farkas *et al.*, 2000, 2003; Foster *et al.*, 2000; Murphy *et al.*, 2007; Zhang *et al.*, 2012). On the other hand, some studies record no seasonal changes in Hg concentrations (Park and Curtis, 1997; Farkas *et al.*, 2000; Foster *et al.*, 2000; Burger *et al.*, 2009).

It is hypothesized that increased growth rates in the fish will lead to reduced mass-specific MeHg concentration by somatic growth dilution (Stafford *et al.*, 2004; Karimi *et al.*, 2007). Some studies have documented that different fish growth rates can contribute to modify Hg concentrations in fish muscle when comparing fish of similar lengths (Simoneau *et al.*, 2005). Furthermore, as fast growing fish during summer assimilate more biomass relative to Hg than slow growing fish, it is assumed that the ingested Hg becomes diluted by a larger body mass. In other words, fish with low activity costs are expected to contain lower levels of Hg in their muscle tissue (Trudel and Rasmussen, 2006). On the other hand, the opposite occurs during the winter period, with little fish growth and higher Hg concentrations (Lindqvist *et al.*, 1991). During this starvation period the fish catabolize their own muscle tissue for energy, reducing the body mass faster than the bound MeHg, with the subsequent increase of the overall Hg concentration in the fish muscle (Cizdziel *et al.*, 2002). Stable isotope analysis of nitrogen (N) and carbon (C) provide a powerful tool for characterizing food web structures in lakes and the pathways of energy flow through the food chain (Post, 2002). While the stable carbon isotope ratio ($\delta^{13}C$) undergoes little fractionation (0.4 ± 1.3‰ per trophic level) with assimilation of food, the stable nitrogen isotope ratio ($\delta^{15}N$) is enriched by about 3.4 ± 1‰ relative to their diet (Post, 2002) and thus, useful for estimating trophic position of organisms (Minagawa and Wada, 1984; Peterson and Fry, 1987; Kling *et al.*, 1992). Consumers feed potentially on many sources, it has been shown that there is a duality of pelagic and benthic production in lakes, and fish are mobile consumers linking both habitats (Vander Zanden and Vadeboncoeur, 2002). Thus, cross-habitat feeding by fish will generate a mixture in their $\delta^{13}C$ signatures; predators potentially feeding on different sources can lie in the same isotopic area (Soto *et al.*, 2013).

The $\delta^{15}N$ signatures of starving or natural fasting animals typically show elevated values (Hobson *et al.*, 1993). Starving (protein-limited) animals catabolize their own bodily proteins to use as energy and amino acid sources. The starvation and the subsequent deamination and transamination (internal rearrangement of N) are isotope fractionation processes, and might be the reason for the high $\delta^{15}N$ values, generating an isotopic enrichment analogous to the process by which the tissues of animals at high trophic levels become ^{15}N enriched (Gannes *et al.*, 1998). Since $\delta^{15}N$ can be used to characterize trophic relationships in aquatic food webs, a simple linear relationship between Hg (with logarithmic transformation) and $\delta^{15}N$ in organisms within a food web can be used to rate the biomagnification power of Hg. The slope of this regression (trophic magnification slope, TMS) has been used in many studies to quantify the biomagnification potential. The trophic magnification factor (TMF) also represents the average biomagnification of a pollutant per trophic level. When TMF > 1 then Hg biomagnifies through the food web (Lavoie *et al.*, 2013).

In our study, we have investigated seasonal variations of Hg concentration (mg kg^{-1} ww) and $\delta^{13}C$ and $\delta^{15}N$ signatures (‰) in muscle tissue from northern pike - *Esox lucius* L, European whitefish - *Coregonus lavaretus* L and European perch - *Perca fluviatilis* L in Lake Heddalsvatn, southern Norway. As the captured fish represent various trophic levels from piscivorous to planktivorous or benthivorous fish, seasonal variations of Hg are studied both within and between fish species.

METHODS

Site description

Lake Heddalsvatn (59° 33′ N, 9° 13′ E) is located in the county of Telemark, southern Norway. The lake is a relatively big (surface area: 13.39 km^2; lake volume: 0.44 km^3), medium deep (maximum depth: 54 m; medium depth: 37 m) lake, located at 16 m asl, with a large catchment (5 036 km^2). The lake is surrounded partly by mountain and woodland areas as well as some agricultural areas. The city Notodden (13 000 inhabitants) is situated in the northern end of the lake. Two main rivers flow into the lake from north, the River Heddøla and the River Tinnelva, the latter draining large parts of the Hardangervidda, a large high mountain plateau.

Historically, a potential local Hg source was a paper mill operating at the outlet of River Tinnelva until 1972. In addition, Hg has also been used as a fungicide in the surrounding agricultural areas, until prohibited in 1990. Today, the main known Hg source in remote areas, as in the Heddalsvatn area, is the long range atmospherically transported air-pollution Hg (Ranneklev *et al.*, 2009).

Sampling

Samples were collected over three seasons, December 2008, May 2010 and September 2010. The fish were caught by gillnets of different mesh sizes (from 10 mm to 52 mm) in order to cover a representative selection of various length and age classes of the 3 fish species investigated. Due to this fishing method the sampling replicates was not balanced between seasons and fish species. The fishing was conducted only in the northern part of Lake Heddalsvatn, a large shallow area, which is not necessarily representative of the entire lake. A total of 266 fish of the 3 species were sampled, 49 pike, 121 whitefish and 96 perch. Pike and whitefish were collected in all three seasons, while we were not able to catch perch in December, a period of the year where this species is very immobile (Borgstrøm and Hansen, 1987). Each fish was stored in individual plastic bags in a freezer (< -18°C) until analyzed for Hg and stable isotopes.

Sample preparation and analysis

Age determinations were mainly done by examination of otoliths. Otoliths were first burned with a butane lighter and then sectioned on the concave side in the center of the otolith. The sectioned pieces were studied under a light microscope. In addition, the metapterygoid bone was dissected for age determination of pike, while the operculum was sampled as a supplementary support for age determination of perch.

Analyses of Hg were conducted on fish tissue taken from the mid dorsal muscle (two duplicates of 100 mg). Hg samples were analyzed by atomic absorption spectrometry, using a RA-915M Mercury Analyzer with a pyrolyzer PYRO-915+ (Lumex Instruments). A tuna fish standard (European Reference Material CE464) with a Hg concentration of 5240 ppb was used for the calibration of the instrument. Prior to stable isotope analyses of N and C, a small dorsal muscle sample was dried in an oven for 24 h at 60-80°C before grounded to fine powder by mortar and pestle. Approximately 1 mg of dried material was then transferred into 9x15 mm tin capsules, and analyzed by the Norwegian Institute of Energy Technology (IFE). All isotope values are referring to primary standards. For C the reference standard, PDB, is marine carbonate, Pee Dee Belemnite (Craig, 1953). For N the reference standard is atmospheric nitrogen (Mariotti, 1983). The relationships between stable isotopes of C and N ($\delta^{13}C = {}^{13}C/{}^{12}C$ and $\delta^{15}N = {}^{15}N/{}^{14}N$) are reported in ‰ and expressed by the following equation:

$$\delta^{15}N \ or \ \delta^{13}C = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) * 1000 \qquad \text{(eq. 1)}$$

where R represents the ratio between the heavy and light isotope, i.e. ${}^{13}C/{}^{12}C$ or ${}^{15}N/{}^{14}N$.

We assumed that consumers become enriched on average by 3.4 ‰ per trophic level (Minagawa and Wada, 1984; Post, 2002). On the other hand, $\delta^{13}C$ signatures are rather weakly enriched as trophic level increases, but they vary in the base of the food chain (Peterson and Fry, 1987). The biomagnification of Hg has typically been calculated with the following equation (eq. 2) (Lavoie *et al.*, 2013):

$$\mathrm{Log[Hg]} = b \cdot \delta^{15}N + a \qquad \text{(eq. 2)}$$

where *b* is the trophic magnification slope (TMS) and *a* is the intercept, previously considered as an estimate of the concentration of Hg that is incorporated at the base of the food web.

The trophic magnification factor (TMF) of the ecosystem is calculated as the antilog of the TMS per trophic level (Lavoie *et al.*, 2013), *i.e.*:

$$\mathrm{TMF} = 10^{(b \cdot 3.4‰)} \qquad \text{(eq. 3)}$$

Statistics

To explain the Hg fluctuations in different seasons we tested the hypothesis of whether growth dilution or the opposite phenomenon caused by starvation/energy expenditures due to spawning/reproduction were the cause for these differences in Hg concentration. Statistical analyses included analysis of covariance (ANCOVA), using the mercury concentrations as the dependent variable, season as a nominal independent factor and length, age, body mass or δ^{15}N as candidates for continuous covariates in the model. The minimum Akaike Information Criterion (AIC) was used to choose the best model. The model residuals were checked for normality, heteroscedaticity and serial correlations. The Mann Whitney test was used for the examination of specific differences of isotopic C burden, both within species and between species. The data were also examined with linear regression analysis for correlations between mercury content and fish size (length or mass), age and stable isotopes for each fish species, with all seasonal data together. A logarithmic transformation of the Hg concentration, length, body mass and age values was used to improve normality of data. The regression residuals were tested for normality and a Durbin Watson test for serial correlations was used.

A significance level of 0.05 was used in the significance tests. All the statistical analyses were conducted by JMP Statistical Software (SAS Institute Inc., 2010) and/or Minitab 16 Statistical Software.

RESULTS

Statistical data on morphology (total length, mass), age, δ^{15}N and δ^{13}C (‰) and Hg (mg kg^{-1} ww) from the 3 fish species investigated in Lake Heddalsvatn at three different seasons (December, May and September) are presented in Tab. 1. The Hg concentrations in the fish from Lake Heddalsvatn varied from 0.04 to 2.50 mg kg^{-1} (ww), with the highest value found in the biggest and eldest individual of pike (112 cm, 9.8 kg and 16 years). The highest average Hg concentrations and most enriched δ^{15}N signatures were found in pike, followed by perch, and with the lowest average values present in whitefish.

The $\delta^{15}N$ signatures were significantly higher ($P<0.05$) in May and December compared with September for all three species, except for the fact that we have no fish data for perch in December. The $\delta^{15}N$ signatures in December and May were relatively similar. The TMS in the northern part of Lake Heddalsvatn for all fish species and seasons was 0.19±0.02. The Hg concentration was calculated to increase by a factor (TMF) of 4.29 per trophic level in the lake food web. The TMS including all fish species for the months of May, September and December was 0.27±0.04, 0.14±0.03 and 0.15±0.04, respectively. There were not significant ($P>0.05$) differences in the $\delta^{13}C$ signatures between species nor between seasons within a species. However, $\delta^{13}C$ in whitefish had a significantly higher variance than pike and perch, which might reflect a broader ecological niche with regard to carbon sources (zooplankton, terrestrial surface insects and zoobenthos). During all seasons, significant positive correlations existed between Hg concentration in muscle tissue and length, body mass, age, and $\delta^{15}N$ in perch and pike (Tab. 2), except for the correlation between Hg and $\delta^{15}N$ in pike in September ($P=0.099$). For whitefish, also significant positive correlations existed between Hg concentration in muscle tissue and length, mass and age, while regarding $\delta^{15}N$, a significant positive correlation ($P=0.006$; $R^2=18.0$) with Hg was only found in September (Tab. 2).

The covariance analysis for perch showed that both length and age contributed to the variation in Hg concentrations (all variables log-transformed) together with season (Fig. 1, Tab. 3). The model was highly significant ($P<0.0001$) and explained 81% of the variations in log Hg concentrations. Length was the most important explanatory variable ($F_{1,92}$ =35.8, $P<0.0001$), followed by age ($F_{1,92}$ =10.3, $P=0.002$) and season ($F_{1,92}$ =7.0, $P=0.01$). No significant interactions between season and length or age could be proved, hence the effect of length and age did not differ between seasons. The $\delta^{15}N$ values did not provide any further significant contribution to the model ($P=0.23$). The concentration of Hg in perch was significantly higher in May 2010 (0.35 mg kg^{-1}) than in September 2010 (0.26 mg kg^{-1}) after adjusting to geometric mean length (22.8 cm) and age (4.4 yr). The perch caught during September 2010 were significantly bigger (23.4 cm, 169 g) compared to those caught in May 2010 (21.1 cm, 125 g) after adjusting for differences in age distribution. There was no significant variation ($P<0.0001$) in the length-mass relationship between seasons, maintaining the same mass at a given length (May: 158 g and September: 154 g).The covariance analysis between Hg concentrations in pike and length (both log-transformed) for different seasons showed that the interaction between length and season was insignificant ($P=0.43$), indicating parallel regressions of Hg concentration on length (both log-transformed) for the different seasons (Fig. 2, Tab. 3). The model was highly significant, explaining 84% of the variation in log Hg concentrations ($P<0.0001$). Length was the most important variable ($F_{1,44}=131.8$, $P<0.0001$), whereas the effect of season was close to significance ($F_{2,44}=2.74$, $P=0.07$). Neither $\delta^{15}N$ nor age (log-transformed) could provide any further significant contribution to the model (P= 0.99 and 0.26, respectively).The length-adjusted Hg mean for pike, adjusted to geometric mean length (48.9 cm) was higher in December 2008 (0.60 mg kg^{-1}) than in May and September 2010 (0.47 and 0.43 mg kg^{-1}, respectively). A *post-hoc* test (least square means contrast) indicated that the length adjusted Hg mean of December 2008, could be significantly higher than that of May and September 2010 ($P=0.02$). For the two different seasons in 2010 (May-September) the pike length at a given age (average: 4.8 yr) was slightly shorter ($P=0.04$) in September (46.2 cm) compared with May (52.2 cm). However, there were not significant ($P=0.2$) variations in the length-mass relationships between May (637 g) and September (669 g), maintaining the same condition in both months. For whitefish the covariance analysis showed that the most important factor for Hg variations is the age. The interaction between age and season was insignificant ($P=0.45$), indicating parallel regressions for the different seasons (Fig. 3, Tab. 3). The model between Hg concentration and age (both log-transformed) for different seasons was significant (P 0.0001) and explained 49% of the Hg variations. The effect of the age was the most important factor ($F_{1,116}=50.38$, $P<0.0001$) followed by the effect of season ($F_{2,11}=9.77$, $P=0.0001$). Neither $\delta^{15}N$ nor length (log-transformed) could provide any further significant contribution to the model (P= .86 and 0.24, respectively). The concentration of Hg in whitefish at a given age (average: 6.1 yr) was significantly higher in December 2008 (0.16 mg kg^{-1}) compared with May 2010 (0.12 mg kg^{-1}) and September 2010 (0.11 mg kg^{-1}), while the difference between May and September was not significant. However, significant seasonal mass-length relationship was revealed, as the whitefish in May 2010 (306 g) were significantly heavier at a given length compared with September 2010 (284 g) and December 2008 (254 g). There was a large variation in $\delta^{13}C$ signatures in the investigated whitefish (-23.9‰ to -32.7‰), but not significant variations between the seasons.

DISCUSSION

In boreal areas, like in Scandinavia, little fish data exist from the cold and normally snow rich winter periods, when most lakes are covered by ice. he cold and dark environment present at that time of the year implies minor biological production at all ecosystem levels. Accordingly, the activities of many fish species, including feeding activity, are at minimum (Greenfield *et al.*, 2005) and variuous degrees of starvation likely appear in the fish populations. Conversely, during the growth season (May-October), feeding activity, growth rate and growth efficiency are high (Lindqvist *et al.*, 1991), and the body mass of the fish increases rapidly (Talbot, 1993). Consequently, seasonal variations in Hg concentrations and δ^{15}N in fish should be expected as these parameters are expected to respond to variations in growth (decrease in Hg and δ^{15}N) and starvation (increase in Hg and δ^{15}N). The evaluation of seasonal variations of Hg concentrations in fish from our study was implemented in different years, 2008 and 2010. We assumed that there was no influence on the interpretation of the data regarding temporal variation from the year 2008 to the year 2010, and that the seasonal variations have a stronger influence on the fish Hg concentrations. Braaten *et al.* (2014) tested temporal variations on THg and MeHg concentrations in three boreal lakes and showed a minimal but not significant variation within the two years of their study (2010-2012). Major watershed disturbances (such as forest fires or clearcutting) or local point sources of pollution would imply a possible variation in inter-annual concentrations of Hg, but such events have not occurred in lake-near areas during the investigated period.

There exist differences in fish Hg concentrations between sexes and these differences have primarily been attributed to energy expenditures during the spawning season and growth rates (Gewurtz *et al.*, 2011; Stacy and Lepak, 2012). Sex determination was not conducted in our study; however, as the Hg concentrations were normalized to body mass and/or length when comparing between seasons, we assumed that it is indirectly accounting for possible sex-specific differences. The TMS obtained in our study (0.19) is comparable to a recent report throughout different regions and ecosystems worldwide, which shows mean values of 0.16±0.11 for total Hg and 0.24±0.08 for MeHg (Lavoie *et al.*, 2013). The comparison of the TMS values during different months could lead to misinterpretations due to the unbalanced replication of samples in the different seasons, which may influence the slope and the TMF. The regression may as well be substantially influenced by the number of trophic levels included in the samples (Borgå *et al.*, 2012), which varies greatly between each season sampled in the study. There was no significant species specificity in the δ^{13}C signatures. The average δ^{13}C signatures for all fish species in our study lake (Tab. 1) have typical values for energy sources derived from pelagic areas (-28,4‰; Vander Zanden and Rasmussen, 1999). However, it is well-known that fish are a mobile species and integrate both pelagic and benthic food webs in lakes and they derive energy opportunistically from both habitats (Post *et al.*, 2000b; Vander Zanden and Vadeboncoeur, 2002). Unfortunately, prey organisms were not sampled to estimate the percent contribution from littoral or pelagic sources to each individual. Stable isotope signatures of fish that feed on different food sources may lie in the same isotopic position while truly belonging to different niches. Hence, it is a tentative assumption to only consider measured δ^{13}C signatures of the fish to assess their energy sources. Therefore, δ^{13}C did not add explanatory power to the description of Hg concentrations within the food web of the lake.

Our data confirm seasonal variations in the Hg concentrations in fish from Lake Heddalsvatn, but the causes may vary depending on fish species. Generally, the highest concentrations of Hg and δ^{15}N in muscle tissue of fish (only pike and whitefish caught) were observed during winter time (December). Perch showed clear seasonal variations in the Hg concentrations. After the spawning in late April–May, the fish population increased in mass rapidly throughout the summer with subsequent decrease in the Hg concentration in muscle tissue. The most likely explanation is the somatic growth dilution of Hg, as also shown by Stafford *et al.* (2004), where Hg concentrations decreased with fish growth. Our results also concurred with the seasonal Hg patterns described by Meili (1991) in Swedish lakes, where the Hg concentrations were higher during May compared to September for all fish species investigated (pike, perch and roach). Both length and age were important explanatory factors for the Hg concentrations in the perch population, indicating the tight relationship between bioenergetics and Hg accumulation in fish (Trudel and Rasmussen, 2006). It is hypothesized that Hg concentration increases over time when the uptake rate of Hg exceeds the sum of excretion rate and growth dilution rate. That is, older fish will have higher Hg concentrations than younger fish at a given length. An old fish has had a longer exposure time to accumulate Hg than a young fish, even though both have achieved the same length. This phenomenon is more pronounced in populations with individuals with a stagnated growth pattern or in older individuals that have reduced growth efficiency, due to the fact that metabolic costs are relatively higher in older individuals (Trudel and Rasmussen, 2006). The seasonal changes of Hg in muscle tissue of pike could not be explained by growth dilution, since there was no measurable growth from May to September in the fish caught. An explanation might be the single capture site within a restricted area of the lake, which may have biased the results. In large and deep lakes, whitefish might represent various sub-populations of different phenotypes occupying specific niches (Harrod *et al.*, 2010), but all sub-populations basically feed on zooplankton and benthos. This likely explains the very low concentration of Hg in all three investigated seasons. Despite so, seasonal variations of Hg in whitefish were documented. However, this cannot be explained by growth dilution since the fish caught in September at the end of the growth season, were smaller than those caught in May. Based on our data, no adequate reasons for this fact can be found. The wide range in $\delta^{13}C$ in whitefish (-23.9‰ to -32.7‰), which indicates large variation in habitats and/or feeding strategy, may have influenced on the results. Additionally, similar $\delta^{13}C$ signature variations in whitefish have been found in Lake Norsjø, the first downstream lake from Lake Heddalsvatn (Jensen, 1954; Moreno and Lydersen, 2014). The higher $\delta^{15}N$ signatures found in fish in Lake Heddalsvatn in December and May compared with September, concur with a previous study by Gannes *et al.* (1998) where they affirm that the processes by which the tissues of animals at high trophic levels become enriched in $\delta^{15}N$, probably apply to starving animals. As May and December belong to cold and dark winter-period in lakes at high latitudes, minor biological activity and production occur. Accordingly, the feeding rates of fishes are at minimum, and starvation with subsequent $\delta^{15}N$ enrichment might occur. However, the significant seasonal variations in $\delta^{15}N$ in all three species in our study were mainly related to fish body size variations. For pike and perch, the lower $\delta^{15}N$ signatures in September were associated with a decrease in mean fish size. For perch, the decrease from May to September also coincided with a decrease in mean fish size. There were no significant differences in the length adjusted seasonal means in $\delta^{15}N$ for pike and whitefish ($P>0.05$), whereas a small statistical significant reduction from May to September ($\Delta^{15}N$ = -0.7 ‰) could be detected for perch ($P=0.02$).

In Norway, the human consumption limit for fish is 0.5 mg Hg kg^{-1}(ww) in muscle tissue of perch and whitefish and 1.0 mg Hg kg^{-1} regarding pike (Codex-Alimentarius-Comission, 1991). Predicted results by linear regression analyses, showed that bigger individuals of pike (100 cm, 9.0 kg) and perch (27 cm, 0.302 kg) are needed to exceed this limit in September, compared with fish caught in May (pike: 79 cm, 3.6 kg; perch: 24 cm, 0.187 kg). As only a few individuals of pike and no perch were caught in December, these data are not incorporated in this comparison. For the planktivorous and benhtivorous whitefish, the concentrations of Hg are generally well below these limits during all seasons.

CONCLUSIONS

The investigation of pike (piscivorous), whitefish (planktivorous, benthivorous) and perch (generalist) in Lake Heddalsvatn has documented seasonal variations in the muscle tissue Hg concentrations, disregarding confounding factors such as fish length, age or $\delta^{15}N$ signatures. However, length was the most important explanatory variable for Hg concentrations in fish tissue from pike, while age was the most important factor for whitefish. Both length and age combined were the best explanatory factors for perch.

The highest Hg concentrations were revealed in the fish species caught in December (pike and whitefish). The Hg concentrations in May were higher than in September for all 3 species, it was of statistical significance for perch and close to significant for pike. The interplay between low feeding rates during the winter (starvation) and somatic growth dilution during summer is likely the main factor for seasonal Hg fluctuations in fish in high latitude lakes as Lake Heddalsvatn. For perch, this was the main explanation for the Hg seasonal variations. Regarding whitefish, it is well known that several subpopulations occur in the lake, varying in size, condition factor, and use of littoral habitat for feeding and/or spawning. Despite so, a significant positive correlation was found between Hg in muscle tissue of whitefish and age, and that the Hg concentrations differed between seasons.

Due to seasonal variations of Hg in fish from Lake Heddalsvatn, bigger perch and pike can be eaten during autumn before the consumption limits of 0.5 mg kg^{-1} (perch) and 1.0 mg kg^{-1} (pike) are reached, while Hg in all whitefish was below these limits.

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Tab. 1. Summary data for the length, mass, age, total Hg concentration, measured $\delta^{13}C$ and $\delta^{15}N$ in muscle tissue for the three fish species in Lake Heddalsvatn, southern Norway.

Species (n)	Season (n)	Statistics	Length (cm)	Mass (g)	Age (yr)	Hg ppm(ww)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
Pike (49)	May (23)	Mean±sd	57.1±16.7	1581±1227	6±2	0.64±0.33	-27.8±0.7	9.5±1.1
		Median	58.9	1320	5	0.58	-27.7	9.4
		Min-max	27.5-87.0	125-4250	3-10	0.15-1.30	-29.3- -27.0	7.8-11.7
	Sept. (18)	Mean±sd	39.9±14.5	619±808	4±2	0.34±0.20	-27.8±0.9	8.2±1.4
		Median	35.8	277	4	0.27	-28.0	8.5
		Min-max	25.0-77.0	52-3060	2-7	0.16-0.86	-29.4- -25.9	3.6-10.1
	Dec. (8)	Mean±sd	63.3±24.4	2661±3009	7±4	0.95±0.74	-28.4±1.4	9.5±1.7
		Median	64.8	2000	6	0.76	-28.0	9.7
		Min-max	26.3-112.0	111-9800	2-16	0.07-2.50	-31.6- -27.2	6.3-11.7
Whitefish (121)	May (24)	Mean±sd	34.6±5.4	471±316	7±3	0.15±0.07	-27.5±1.3	8.7±0.5
		Median	33.6	367	6	0.14	-27.9	8.7
		Min-max	28.3-50.0	208-1609	3-15	0.06-0.38	-29.8- -24.5	7.7-9.9
	Sept. (41)	Mean±sd	27.0±5.5	194±152	4±2	0.10±0.04	-27.8±1.3	8.0±0.7
		Median	25.5	123	4	0.09	-28.1	7.9
		Min-max	19.5-44.0	54-743	2-11	0.04-0.21	-30.7- -23.9	6.7-9.7
	Dec. (56)	Mean±sd	35.5±7.1	456±303	7±4	0.23±0.28	-28.2±1.9	8.7±0.9
		Median	34.7	310	6	0.15	-28.3	8.7
		Min-max	21.4-48.7	65-1245	2-22	0.07-2.07	-32.7- -24.0	5.6-11.0
Perch (96)	May (26)	Mean±sd	25.2±3.4	244±109	6±1	0.68±0.33	-27.6±0.7	9.2±0.7
		Median	25.6	228	7	0.66	-27.6	9.3
		Min-max	16.3-31.4	45-503	4-8	0.11-1.32	-28.9- -25.5	8.1-10.8
	Sept. (70)	Mean±sd	22.5±4.6	175±128	4±2	0.32±0.31	-27.9±0.9	8.3±1.1
		Median	21.8	120	4	0.18	-27.8	8.5
		Min-max	14.5-32.0	35-567	2-8	0.06-1.33	-31.0- -25.3	4.3-10.5

Tab. 2. Linear regression equations for the relationships between Hg concentration and the length (cm). mass (g). age and stable nitrogen isotope (δ^{15}N) for pike. whitefish and perch. collected during three different months in Lake Heddalsvatn.

Species	Season (n)	Regression equation	R^2	P
Pike	May (23)	LogHg= -2.98 + 1.57·LogLength	82.5	0.000
		LogHg= -1.73 + 0.49·LogMass	80.1	0.000
		LogHg= -1.02 + 1.08·LogAge	79.4	0.000
		LogHg= -1.90 + 0.17·δ^{15}N	59.5	0.000
	Sept. (18)	LogHg= -2.48 + 1.24·LogLength	68.8	0.000
		LogHg= -1.44 + 0.36·LogMass	69.0	0.000
		LogHg= -0.97 + 0.81·LogAge	52.7	0.001
		LogHg= -1.11 + 0.07·δ^{15}N	16.1	0.099
	Dec. (8)	LogHg= -4.34 + 2.35·LogLength	86.7	0.001
		LogHg= -2.57 + 0.75·LogMass	86.7	0.001
		LogHg= -1.26 + 1.37·LogAge	69.2	0.010
		LogHg= -2.37 + 0.23·δ^{15}N	74.6	0.006
Whitefish	May (24)	LogHg= -3.00 + 1.39·LogLength	22.4	0.020
		LogHg= -1.72 + 0.33·LogMass	16.0	0.053
		LogHg= -1.53 + 0.80·LogAge	55.4	0.000
		LogHg= -1.36 + 0.058·δ^{15}N	2.8	0.434
	Sept. (41)	LogHg= -2.81 + 1.25·LogLength	36.5	0.000
		LogHg= -1.83 + 0.36·LogMass	33.5	0.000
		LogHg= -1.39 + 0.62·LogAge	50.3	0.000
		LogHg= -1.80 + 0.096·δ^{15}N	18.0	0.006
	Dec. (56)	LogHg= -2.09 + 0.87·LogLength	9.8	0.019
		LogHg= -1.38 + 0.25·LogMass	10.2	0.016
		LogHg= -1.19 + 0.55·LogAge	24.8	0.000
		LogHg= -1.21 + 0.052·δ^{15}N	2.7	0.230
Perch	May (26)	LogHg= -5.40 + 3.69·LogLength	62.1	0.000
		LogHg= -2.50 + 0.97·LogMass	58.3	0.000
		LogHg= -2.08 + 2.32·LogAge	51.6	0.000
		LogHg= -2.21 + 0.21·δ^{15}N	22.3	0.015
	Sept. (70)	LogHg= -5.67 + 3.73·LogLength	76.3	0.000
		LogHg= -2.98 + 1.08·LogMass	76.9	0.000
		LogHg= -1.76 + 1.88·LogAge	71.0	0.000
		LogHg= -1.88 + 0.15·δ^{15}N	14.3	0.001

Tab. 3. Hg concentration (log) as a function of length (log) and season in pike as a function of age (log) and season in whitefish. and of length. age and season in perch. Parameter estimates (B) with confidence level (CL). standardized parameter estimates (β). significance levels (P) and length or age adjusted means (Hg_{adj}).

Species	Term	B	B. lower 95% CL	B. upper 95% CL	β	P	Hg_{adj} (ppm ww)
Pike	Intercept	-6.333	-7.338	-5.327	0.000	<0.0001	
	Dec. 2008	0.188	0.024	0.351	0.198	0.026	0.60
	May 2010	-0.050	-0.163	0.063	-0.055	0.373	0.47
	Sept. 2010	-0.137	-0.278	0.004	-0.143	0.056	0.43
	Log length	1.448	1.194	1.702	0.830	<0.0001	
Whitefish	Intercept	-2.928	-3.184	-2.672	0.000	<0.0001	
	Dec. 2008	0.199	0.106	0.291	0.333	<0.0001	0.16
	May 2010	-0.050	-0.166	0.066	-0.075	0.397	0.12
	Sept. 2010	-0.149	-0.258	-0.039	-0.258	0.0084	0.11
	Log age	0.522	0.376	0.668	0.533	<0.0001	
Perch	Intercept	-10.254	-12.338	-8.171	0.000	<0.0001	
	May 2010	0.155	0.039	0.271	0.148	0.001	0.35
	Sept. 2010	-0.155	-0.039	-0.271	-0.148	0.001	0.26
	Log length	2.548	1.702	3.393	0.541	<0.0001	
	Log age	0.740	0.283	1.197	0.326	0.002	

Pike, Hg adjusted to geometric mean length: 48.9 cm. Analysis of covariance: R^2 =0.84; P<0.0001. Whitefish, Hg adjusted to geometric mean age: 6.1 yr. Analysis of covariance: R^2 =0.49; P<0.0001. Perch, Hg adjusted to geometric mean length and age: 22.8 cm. 4.4 yr. Analysis of covariance: R^2 = 0.81; P<0.0001.

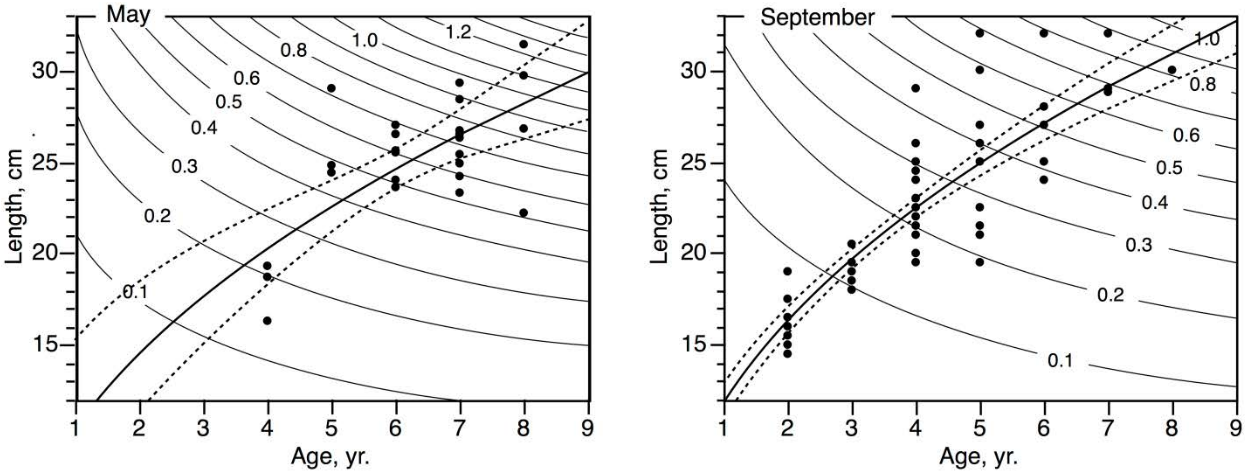

Fig. 1. Contour plots of mercury concentration (mg·kg-1) in perch in May (left plot) and September (right plot) as a function of length and age (log-transformed variables). The plots are based on an ANCOVA model. Growth curves (with 95% confidence interval) are superimposed on the plots (linear regressions on log-transformed variables).

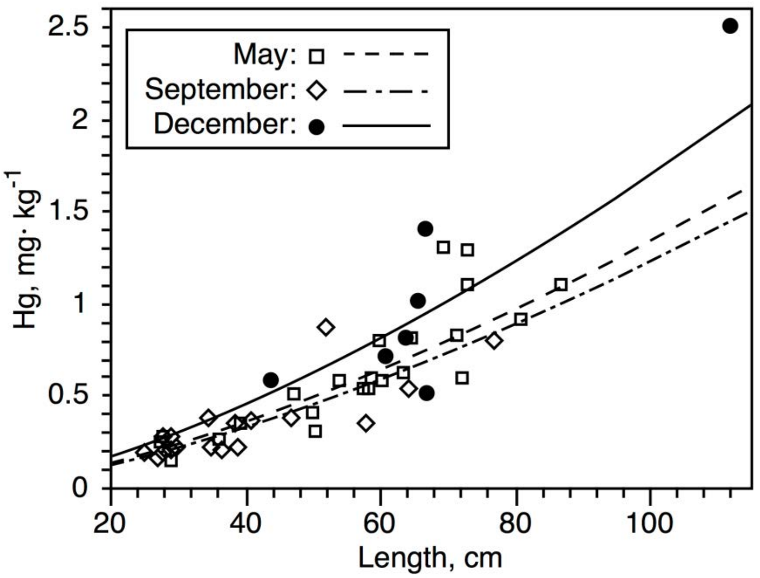

Fig. 2. Hg concentrations in pike as a function of length and season. The regression lines are based on an ANCOVA model (log-transformed variables).

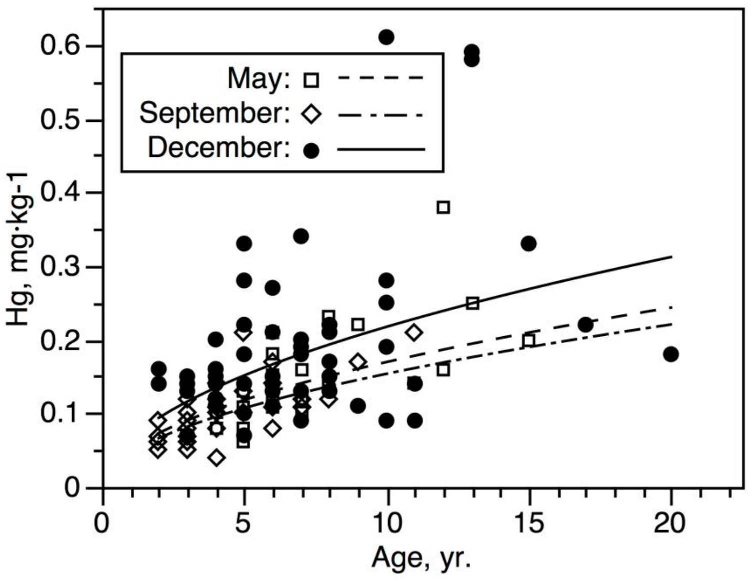

Fig. 3. Hg concentrations in whitefish as a function of age and season. The regression lines are based on an ANCOVA model (log-transformed variables).

Paper IV

The effects of wildfire on the water chemistry of dilute, acidic lakes in southern Norway

Espen Lydersen, Rolf Høgberget, Clara E. Moreno, Øyvind A. Garmo & Per Christian Hagen

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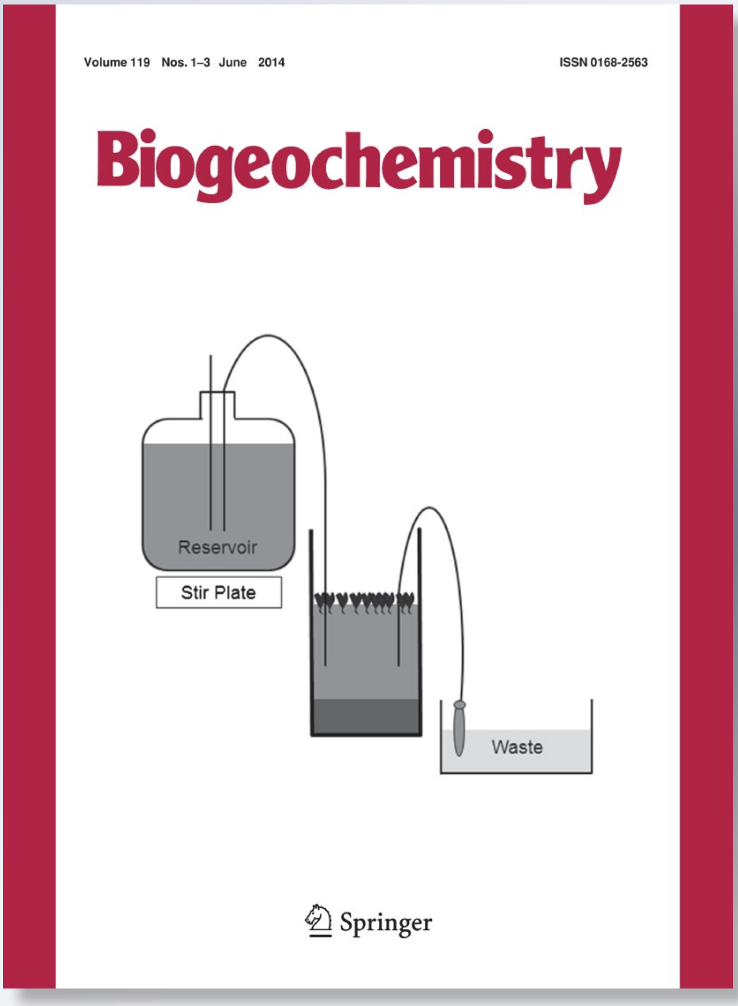

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The effects of wildfire on the water chemistry of dilute, acidic lakes in southern Norway

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Abstract Changes in lake water chemistry were studied for >4 years following a large wildfire in a boreal forest area in Mykland, southern Norway, an area characterized by thin and patchy, base-poor and slow-weathering soils and bedrock. Accordingly, the lakes have low acid neutralizing capacity (ANC), calculated as the difference between the total concentration of base cations ([ΣBC]) and strong acid anions ([SAA]). During the initial post-fire period, and peaking about two months after the fire, the mobilization of SAA from terrestrial to aquatic systems caused a dramatic drop in ANC. In one of the lakes, ANC dropped from about 20 to −80 μeq L^{-1}, while [H^+] and inorganic aluminum ([Al_i]) increased to 38 μeq L^{-1} (pH 4.42) and 326 μg Al L^{-1} (36.2 μeq L^{-1} as Al^{3+}), respectively. Sulfate and chloride were the predominant anions responsible for this decline in ANC, as the nitrate increase was small. After the severe chemical episode, [SAA] in the lakes declined faster than [ΣBC], and within about one year after the wildfire, ANC was back to almost pre-fire values. However, despite the fact that [SAA] also continued to decline faster than [ΣBC] the following years, no further increase in ANC was documented. The strong ionic strength decline and the increase in TOC during the same period have likely counteracted for the potential ANC increase. There were large lake-to-lake variations in water chemistry of the wildfire affected lakes. Hydrology, geology, lake residence time and the catchment area to lake area ratio are important explanatory factors.

Keywords Wildfire · Climate change · Lake water chemistry · Acidification · Southern Norway

Introduction

Wildfire poses a threat to life, property, infrastructure and natural resources in fire-prone areas. Each year wildfires burn large areas of forest land around the world (Smith et al. 2011). Recent projections of future climate changes for the interior of many continents suggest an increase of air temperature by 2–6 °C

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coupled with a 10–30 % decrease of summer precipitation (e.g. IPCC 2001; Schär et al. 2004). An increase in drought is directly related to an increase in wildfire occurrence (e.g. Ryan 2000; Flannigan and Wotton 2001). Thus, the question arises where and how much various areas on earth will be affected by these potential changes.

Prolonged drought followed by a strong rain event, may lead to severe water chemical conditions. In Norway Huitfeldt-Kaas (1922) documented mass death of salmon and brown trout during such an event in 1920. Later, many scientists have dealt with this phenomenon (Jeffries et al. 2003; Laudon et al. 2004; Aherne et al. 2006). Drought periods result in lower water table in wetlands and soils, leading to oxidation of previously stored, reduced sulfur (S), and subsequent efflux of oxidized S (SO_4^{2-}) upon re-wetting. In acid sensitive areas with high sulfur input and low acid neutralizing capacity, severe episodic acidification of surface waters may occur as H^+ and cationic Al (Al^{n+}) appear as predominant counter ions for SO_4^{2-} (Dickson 1978; Cronan and Schofield 1979).

Besides drought, the fire itself is also an oxidation process, which under sufficient oxygen conditions, oxidizes organic carbon to CO_2, organic S to SO_2 and organic N to NO_x, similar to combustion of biofuels. These gases are emitted to air, and after various physical and chemical transformation processes in the atmosphere, they precipitate as acid rain elsewhere, as carbonic acid, sulfuric acid and nitric acids. The combustion remains, left in the wildfire area are mineralized, alkaline ash products, rich in base cations, phosphate, chlorides, heavy metals (Eriksson et al. 2003; Kelly et al. 2006) and pyrolytic polycyclic aromatic hydrocarbons, PAH (Finkelstein et al. 2005).

Wildfire leads to increased runoff (Schindler et al. 1980; Bayley et al. 1992b), mainly due to reduced evapotranspiration. Particle transport to surface waters also increases, due to both increased runoff and increased erosion (Beaty 1994; Karr et al. 2004). Higher turbidity will temporarily increase the light extinction coefficient and water transparency during flood episodes. These effects are very dependent on time after the wildfire, as the increased particle load to surface water declines rapidly, while total organic carbon (TOC) gradually increases again as new allochthonous material is produced (Carignan et al. 2000). The first period after wildfire, the primary production may also affect these parameters, due to the increased supply of N, P and base cations to lakes following wildfire (Planas et al. 2000).

Increases in major base cations, strong acid anions, ammonia, total N and total P in surface water have been reported from many wildfire studies (Schindler et al. 1980; Lamontagne et al. 2000; Carignan et al. 2000; Bayley et al. 1992a, b; Eriksson et al. 2003). Studies documenting significant reduction in pH and ANC (Bayley et al. 1992b; Eriksson et al. 2003) are related to areas with natural base-poor soils and low weatherable rocks. Some of the severe acidification reported from a wildfire in Sweden (Eriksson et al. 2003) is attributed to use of brackish water for firefighting, causing an additional sea-salt effect, an acidification phenomena well described earlier (Hindar et al. 1994; Lydersen and Henriksen 1995; Nystroem et al. 1995).

In this paper we report water chemical effects on six lakes in a very acid sensitive area of southern Norway, impacted by a large wildfire in June 2008. Both short-term and long-term chemical effects (>4 years) of the wildfire on lakes were studied.

Materials and methods

The wildfire area was located in Froland municipality, Aust-Agder county, southern Norway, (Fig. 1). The wildfire started on June 9, 2008 and lasted 1 week. Almost 2,600 ha of forest and wilderness were almost totally damaged, and 120,000 m^3 of forest were lost. Six lakes investigated were within the wildfire area, while three reference lakes were located nearby the impacted area. The control lakes were primarily selected according to the following criteria:

- Proximity to the wildfire affected area
- Negligible influence by land-use and silviculture
- Accessibility by road for use of boat

During the investigated period, powdered limestone was unexpectedly dumped into a stream entering Lake Svarttjenn in September 2009, with significant effects on Ca^{2+}, pH and alkalinity both during 2009 (Table 1) and 2010. Another control lake, Lake Melestjenn showed unusually high concentrations of Na^+ and Cl^-, due to sporadic road salting at icy conditions during the winter (Table 1). The remaining control lake, Lake Jordtjenn has not been significantly affected by human activities during the monitoring

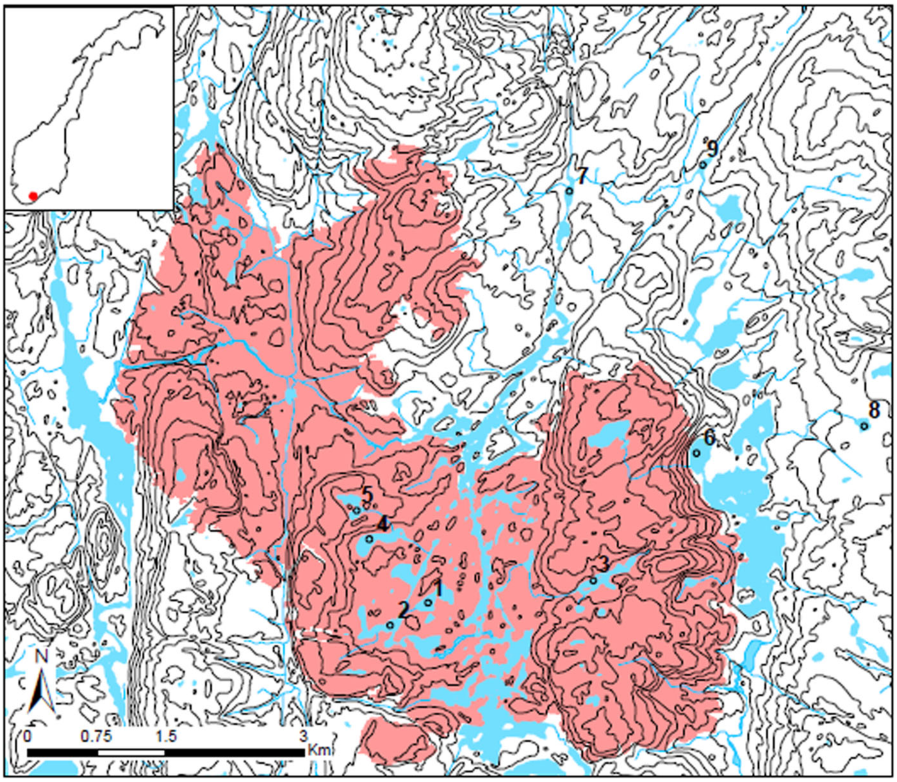


Fig. 1 Map of the wildfire area (*red*) in Mykland, Aust-Agder County, Norway, showing locations of the studied lakes inside (1–6) and outside (7–9) the wildfire area. *Open circles* indicate the sampling site in the lakes. 1: Lake Fisketjenn, 2: Lake Hundsvatn, 3: Lake Øyvatn, 4: Lake Grunnetjenn, 5: Lake Heitjenn, 6: Lake Rasvassvatn, 7: Lake Jordtjenn, 8: Lake Svarttjenn, 9: Lake Melestjenn. (Color figure online)

Table 1 Median water chemistry in the control lakes in 2009 and 2012

Parameter	Unit	Jordtjenn 2009	Jordtjenn 2012	Svarttjenn 2009	Svarttjenn 2012	Melestjenn 2009	Melestjenn 2012
H_{25}	mS m^{-1}	1.79	1.88	1.61	1.92	1.82	2.87
H^+	µeq L^{-1}	6.0	2.6	3.2	4.6	3.9	5.1
Ca^{2+}	µeq L^{-1}	47	42	73	46	59	62
Mg^{2+}	µeq L^{-1}	25	28	26	27	26	29
Na^+	µeq L^{-1}	76	65	69	65	93	122
K^+	µeq L^{-1}	9.5	6.9	9.0	5.9	2.8	5.9
NH_4^+–N	µeq L^{-1}	3.2	2.3	3.9	2.3	6.9	3.3
SO_4^{2-}	µeq L^{-1}	43	39	35	32	15	30
Cl^-	µeq L^{-1}	66	72	65	69	99	141
NO_3^-–N	µeq L^{-1}	2.2	1.4	2.6	1.1	3.7	1.9
SO4*	µeq L^{-1}	35	31	27	26	5.0	16
ΣBC*	µeq L^{-1}	85	67	102	62	80	68
TOC	mg C L^{-1}	5.9	6.0	7.1	7.4	7.4	9.9
ANC	µeq L^{-1}	49	29	74	33	67	51
Total-N	µg N L^{-1}	309	305	298	356	488	460
Al_a	µg Al L^{-1}	145	111	122	143	120	170
Al_o	µg Al L^{-1}	103	74	95	108	102	127
Al_i	µg Al L^{-1}	34	35	27	39	26	36

Table 2 Lake water chemistry in the wildfire affected Lake Hundsvatn and Lake Rasvassvatn, during the rain event in August 2008, compared with the nearby long term monitoring site at Birkenes, and the water chemistry in the same wildfire affected lakes and the least anthropogenic affected control lake, Lake Jordtjenn, in August 2012, >4 years after the wildfire

Parameter	Unit	Hundsvatn	Rasvassvatn August 2008	Birkenes	Hundsvatn	Rasvassvatn August 2012	Jordtjenn
H^+	$\mu eq\ L^{-1}$	38	17	20	3.8	4.2	1.4
Ca^{2+}	$\mu eq\ L^{-1}$	146	60	28	26	20	42
Mg^{2+}	$\mu eq\ L^{-1}$	114	63	16	26	30	30
Na^+	$\mu eq\ L^{-1}$	125	84	118	48	48	57
K^+	$\mu eq\ L^{-1}$	70	33	1.0	4.4	9.5	6.1
$NH_4{}^+$	$\mu eq\ L^{-1}$	19	11	0.4	0.7	0.7	2.1
$SO_4{}^{2-}$	$\mu eq\ L^{-1}$	367	160	55	31	50	31
Cl^-	$\mu eq\ L^{-1}$	165	114	116	65	68	73
$NO_3{}^-$	$\mu eq\ L^{-1}$	2.8	5.4	1.2	0.7	5.7	1.7
ΣBC*	$\mu eq\ L^{-1}$	272	115	35	32	32	54
SO4*	$\mu eq\ L^{-1}$	350	149	43	25	43	24
TOC	$mg\ C\ L^{-1}$	5.0	2.6	7.1	6.4	3.6	6.0
ANC	$\mu eq\ L^{-1}$	−80	−39	−9	7	−17	29
Tot-N	$\mu g\ N\ L^{-1}$	710	445	235	276	248	259
Al_a	$\mu g\ Al\ L^{-1}$	368	295	310	77	79	74
Al_o	$\mu g\ Al\ L^{-1}$	42	22	141	51	42	55
Al_i	$\mu g\ Al\ L^{-1}$	326	273	169	27	37	19

period, until the winter 2011/2012 when a substantial clear-cut was conducted, but chemical lake effects of this logging have so far not been detected (Table 1).

There are no pre-wildfire water chemistry data from the 6 affected lakes and the 3 control lakes. We thus compared the initial wildfire effects on lakes with a nearby long-term monitoring site, Birkenes, located about 31 km southwest from the wildfire area. At this site, dry and wet deposition has been monitored daily by the Norwegian Institute for Air Research, while freshwater has been monitored weekly by Norwegian Institute for Water Research since the early 1970s.

As the Birkenes site is located closer to the sea (20 km from the coast) compared with the wildfire area (about 50 km from the coast), the comparison of Na^+ and Cl^- with Birkenes is omitted. In addition, the low acid neutralizing capacity (ANC) at Birkenes, implies generally lower pH and higher concentrations of inorganic Al (Al_i) at this site compared to the expected pre-fire levels in the wildfire affected area (Table 2). Despite these limitations, it was of interest to compare the chemical effects of wildfire on lakes in Mykland area with the Birkenes site, as this site historically has been the most acid rain impacted monitoring site in Norway. Thus, we decided to use Lake Jordtjenn and the Birkenes site as the main reference sites for the comparison with the wildfire affected sites.

Site description

Since the main lakes in the wildfire area have been artificially limed, we decided to only investigate wildfire affected lakes located upstream the limed lakes. The lakes are located between 229 and 464 m a.s.l., and all lakes drain to the River Tovdal, the cradle of acid rain research in Norway (Drabloes et al. 1980; Sevaldrud et al. 1980). Average annual precipitation in the area is 1,150–1,200 mm and average evapotranspiration 30–36 %. The residence time of the lakes varied from 0.059–3.2 years (Table 3). The catchments of all wildfire affected lakes investigated were totally located within the wildfire area (Fig. 1), except for Lake Rasvassvatn, where ≈10 % of the catchment was outside the wildfire area.

Lake Heitjenn, Lake Fisketjenn and Lake Øyvatn are all headwater lakes. Lake Grunnetjenn and Lake Hundsvatn are the first and second downstream lakes

Table 3 Lake and catchment characteristics of the studied lakes

Lake	Unit	Burnt lakes							Reference lakes	
		Fisketjenn	Hundsvatn	Øyvatn	Grunnetjenn	Heitjenn	Rasvassvatn	Jordtjenn	Melestjenn	Svarttjenn
Latitude		N58 36.549	N58 36.413	N58 36.675	N58 36.906	N58 37.073	N58 37.446	N58 38.956	N58 37.598	N58 39.118
Longitude		E8 17.194	E8 16.770	E8 19.037	E8 16.515	E8 16.370	E8 20.165	E8 18.721	E8 22.063	E8 20.220
Altitute min	m asl	229	228	255	231	271	173	228	222	191
Altitude max	m asl	245	320	316	293	288	360	464	243	464
Lake area (LA)	km^2	0.56	0.15	0.072	0.068	0.037	0.89	0.024	0.0091	0.021
Maximum depth	m	5.8	13	3.2	3.2	2.5	15	9.5	6.2	6.7
Lake volume	1,000 m^3	109	648	77	72		4.6	75	19	46
Catchment area (CA)	km^2	0.23	2.6	1.1	0.86	0.14	1.2	2.9	0.13	6.9
Draining ratio (CA:LA)		4.1	18	15	13	3.8	1.4	122	14	335
Residence time	yr	0.40	0.21	0.059	0.071	0.19	3.2	0.023	0.12	0.058
Lake area (LA:CA)	%	25	5.7	6.6	7.8	26	72	0.82	7.0	0.30
Annual precipitation	mm	1,182	1,184	1,183	1,178	1,165	1,169	1,146	1,184	1,152
Annual discharge	mm	746	753	802	731	742	745	806	781	760
Evapotranspiration	%	36.9	36.4	32.2	37.9	36.3	36.2	29.7	34.0	34.0
Average annual temperature	°C	5.0	4.9	5.0	4.9	4.9	4.9	4.7	5.2	4.8
Agricultural area	%	0.0	0.0	0.0	0.0	0.0	0.0	1.3	5.2	2.0
Bog	%	29.8	22.0	11.8	10.7	3.1	7.8	7.8	8.6	13.3
Lake	%	26.8	12.4	8.1	11.9	26.4	12.5	3.0	15.7	1.8
Forest	%	37.5	61.0	79.3	70.4	52.3	78.2	85.4	62.4	81.7
Naked mountain	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Urban area	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Burnt	%	$\approx$100	$\approx$100	$\approx$100	$\approx$100	$\approx$100	$\approx$90			

Areas impacted by fire (named: Burnt lakes) are also to a certain degree impacted by logging after the wild fire. The three control lakes (named: References) are located in the nearby areas from the wildfire area. Except for lake depth, lake volume and residence time data (own calculations), the data are from the Norwegian energy directorate database

Table 4 Parameters and analytical methods used

Parameter	Unit	Reference
pH	−log[H+]	NS 4720, 1979, 2. Edition
Conductivity	mS m^{-1}	NS-ISO 7888, 1993, 1. Edition
Alkalinity	mmol L^{-1}	NS 4754 (described in Ch.2.3)
Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}	mg L^{-1}	Ionchromatograpy (Dionex IC 1100)
NO_3^-–N, NH_4^+–N	µg L^{-1}	Ionchromatography (Dionex IC 1100)
Total nitrogen	µg N L^{-1}	Persulfate oxidation, FIA: Tecator ASN 110-03/92
Total phosphorous	µg P L^{-1}	NS 4725, 3. Edition, 1984
Total organic carbon	µg C L^{-1}	ISO 1487, TOC analyzer: OI Analytical-1010
Total monomeric Al	µg L^{-1}	Barnes/Driscoll (Barnes, 1975; Driscoll, 1984)
Organic monomeric Al	µg L^{-1}	Barnes/Driscoll (Barnes, 1975; Driscoll, 1984)

from Lake Heitjenn, while Lake Fisketjenn drains into Lake Hundsvatn.

Lake Melestjenn is a headwater lake. Lake Rasvassvatn (173 m a.s.l.) has a headwater lake about 1 km east from the lake, 332 m a.s.l., with its catchment totally influenced by the wildfire. Lake Jordtjenn has a small headwater lake ≈1 km northeast from the lake, and Lake Jordtjenn drains into Lake Svarttjenn.

The wildfire area is characterized by slowly weatherable Precambrian rocks (granites and gneisses), thin and patchy soil cover, often with peat marsh and bogs in the bottom of the valleys and in other depressions of the catchments. Locally some more weatherable, base cation richer bedrocks occur as hypabyssal pegmatite rocks. The vegetation is dominated by various heather species with Norwegian pine (*Pinus sylvestris*) and birch (*Betula pubescens*) as predominant trees, with stands of aspen (*Populus tremula*) on south facing hillsides, and Norwegian spruce (*Picea abies*) in more productive areas.

Precipitation data come from a local weather station at Mykland, just outside the wildfire area, while air temperature data were taken from Nelaug, 17 km east from the wildfire area. Both weather stations are operated by the Norwegian Meteorological Institute.

Sampling and chemical analysis

For two of the wildfire affected lakes, Lake Hundsvatn and Lake Rasvassvatn, water samples were taken on June 25, 2008 (nine days after the fire), on July 9, 2008, during a rain event on August 13, 2008, and on October 30, 2008 (Høgberget 2010), after lake turnover. For Lake Øyvatn, another wildfire affected lake, only one sample was taken in 2008 (on July 16). The control lakes outside the wildfire affected area were not sampled in 2008.

Six lakes within the wildfire area (including Lake Hundsvatn and Lake Rasvassvatn), and three control lakes outside the wildfire area, were monitored monthly from May 19, 2009 to late October 2012. Water samples were collected with a Limnos sampler, transferred to prewashed polyethylene bottles, and stored cold in a darkroom until analyzed. Ion exchange fractionation of aluminum was conducted in field according to Driscoll (1984). Conductivity, pH, alkalinity and Al-fractions were determined within one day after sampled. The analytical methods are given in Table 4.

Calculations

Aluminum (Al) was fractionated according to the Barnes/Driscoll method (Barnes 1975; Driscoll 1984). Two Al-fractions were measured: total monomeric Al (Al_a) and organic monomeric Al (Al_o). Based on these fractions, inorganic monomeric Al (Al_i) was calculated as Al_a–Al_o.

Alkalinity (µeq L^{-1}) was determined by acid titration (with HCl) down to pH 4.5, and the alkalinity was corrected for pH by the following expression:

$$\mathrm{Alk_{corrected}} = \mathrm{Alk_{measured}} - \left([\mathrm{H}^+]_{\mathrm{pH:4.5}} - [\mathrm{H}^+]_{\mathrm{pH:original}}\right)$$

Acid neutralizing capacity (ANC) was calculated on equivalent basis (eq L^{-1}) according to Reuss and Johnson (1986), i.e.:

$$[\mathrm{ANC}]:\ \Sigma\left[\mathrm{Ca}^{2+}\right], \left[\mathrm{Mg}^{2+}\right], [\mathrm{Na}^{+}], [\mathrm{K}^{+}] - \Sigma\left[\mathrm{SO}_4^{2-}\right], \left[\mathrm{NO}_3^{-}\right], [\mathrm{Cl}^{-}])$$

The concentration of non-marine SO_4^{2-} (SO_4*) and non-marine base cations (Ca*, Mg*, Na* and K*) was calculated by subtracting a marine fraction estimated from the ion equivalent ratio to Cl^- in seawater (Weast 1988):

$$\begin{aligned}
\mathrm{SO}_4^* &= \left[\mathrm{SO}_4^{2-}\right] - 0.103[\mathrm{Cl}^-];\\
\mathrm{Ca}^* &= \left[\mathrm{Ca}^{2+}\right] - 0.037[\mathrm{Cl}^-];\\
\mathrm{Mg}^* &= \left[\mathrm{Mg}^{2+}\right] - 0.195[\mathrm{Cl}^-];\\
\mathrm{Na}^* &= [\mathrm{Na}^+] - 0.859[\mathrm{Cl}^-];\\
\mathrm{K}^* &= [\mathrm{K}^+] - 0.0181[\mathrm{Cl}^-]
\end{aligned}$$

As the macro-chemical effects of wildfire on surface waters, basically deals with the relationship between effects of strong acids (basically SO4*) and catchment derived base cations (ΣBC*), much of the macro-chemical interpretation in this paper is based on this non-marine relationship.

Statistics

As the initial water chemical response of wild fire and the subsequent changes during the first post-fire years are very clear for many macro compounds, we have used the Regional Kendall Test (Helsel and Frans 2006) to test for significant post-fire time trends ($P < 0.05$) during the period 2009–2012, i.e. from one to four years after the fire. In this test, the six wildfire affected lakes were defined as one region ("Inside"), while the three control lakes were defined as another region ("Outside"). The Regional Kendall Test provides a median slope and a P value for the time trends significance, and was performed using annual mean values from each lake as input. For other mathematic calculations, Minitab 16 Statistical software program was used.

Results

Initial wildfire effects

After a rain event at the very beginning of May 2008, when 73.5 mm of rain was recorded from April 28 to May 2, only 0.4 mm of rain fell over the Mykland area before the wildfire started on June 9 (Fig. 2).

The first water samples from the wildfire affected lakes were taken June 25, 9 days after the fire was extinguished. Prior to this water sampling, the area had received substantial amounts of rain, i.e. 66 mm (Fig. 2). Compared with the Birkenes site, the first water samples from the wildfire affected lakes, sampled June 25 and July 7, showed significant increases in strong acid anions (SAA), primarily sulfate and chloride, and base cations and ammonia, but only minor changes in pH and inorganic aluminum, Al_i (Figs. 3, 4).

The most extreme water chemical conditions in the wildfire impacted lakes came on August 13, during a strong rain event (119 mm), almost two months after the fire. During this event, non-marine sulfate [SO_4*] in Lake Hundsvatn was 350 μeq L^{-1}, >8 times higher

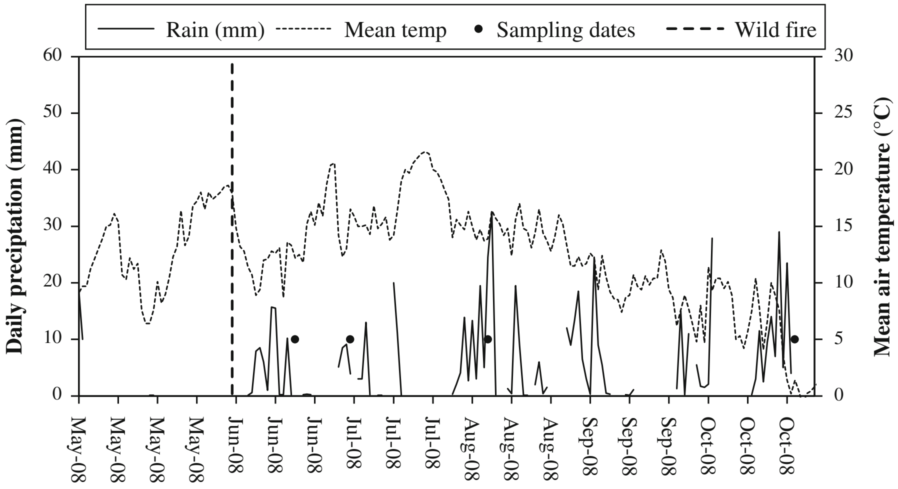
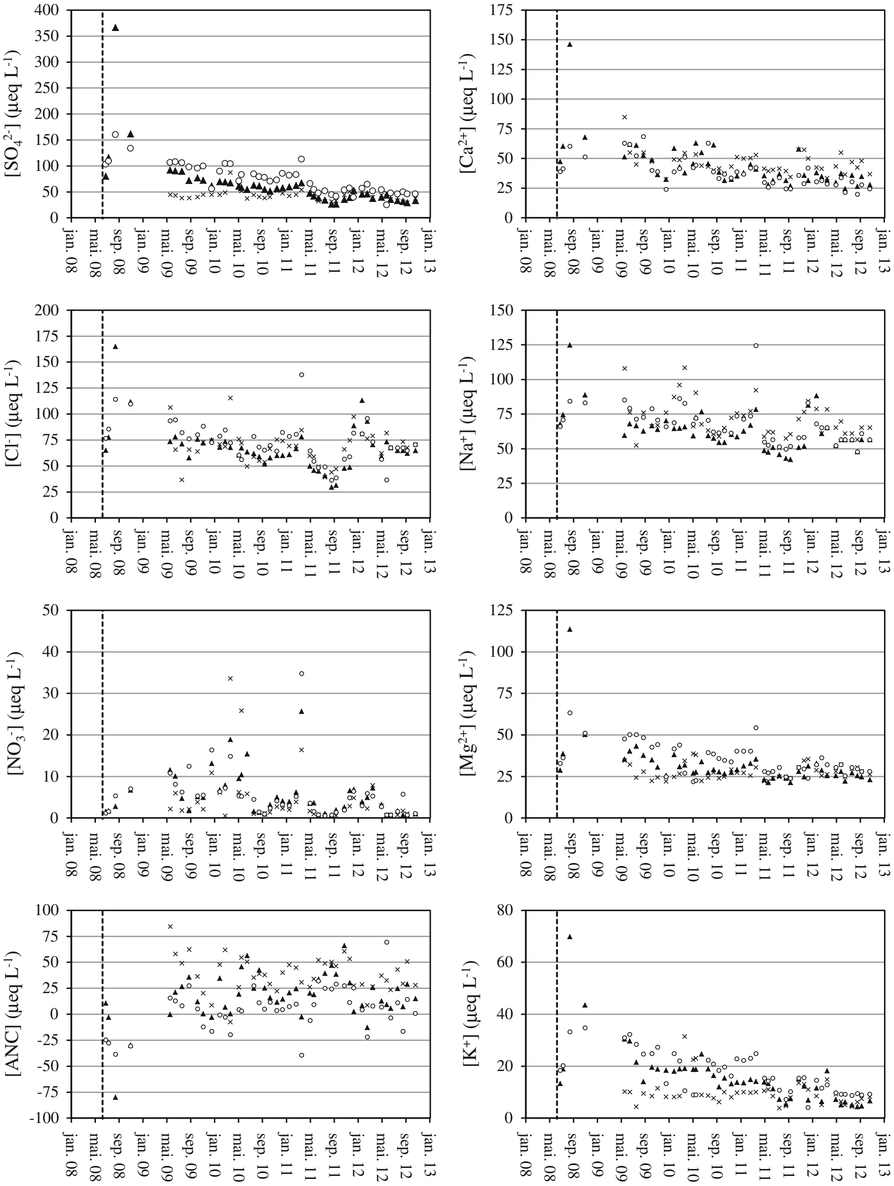


Fig. 2 Daily precipitation (mm) and mean temperature (°C) in Mykland during the period May 1–October 3, 2008. Wildfire period: June 9–June 16

Fig. 3 Concentrations of strong acid anions, base cations and ANC in Lake Hundsvatn *black upper triangle*, Lake Rasvassvatn *white circle*, and the control lake, Lake Jordtjenn *multi sign*, from June 2008 until October 2012. The monitoring started in the control lake in May 2009



than Birkenes. In Lake Rasvassvatn [SO$_4$*] was 149 µeq L^{-1}, 3.5 times higher than at Birkenes (Table 2). Birkenes, the most acid rain impacted monitoring site in Norway, have never shown such high SO$_4$* concentrations since the monitoring started in 1973. Only a few events with [SO$_4$*] >200 µeq L^{-1} have been registered at Birkenes, all of them during the most severe acidification time period, i.e. before 1986 (Fig. 5).

During the August peak, [ΣBC*] in Lake Hundsvatn was 272 µeq L^{-1} (Fig. 5), about eight times higher than at Birkenes (35 µeq L^{-1}), while [ΣBC*] in Lake Rasvassvatn was 115 µeq L^{-1}, >3 times higher than at Birkenes. While the ANC value at Birkenes was −8.8 µeq L^{-1}, ANC was −80 and −39 µeq L^{-1} in Lake Hundsvatn and Lake Rasvassvatn, during this episode (Table 2). The strong decreases in ANC in Lake Hundsvatn caused an almost twofold increase in the concentration of H^{+} and inorganic aluminum (Al$_i$) compared with Birkenes, i.e. 20 µeq H^{+} L^{-1} (pH 4.7) and 169 µg Al$_i$ L^{-1} (19 µeq L^{-1} as Al^{3+}) at Birkenes, compared with 38 µeq H^{+} L^{-1} (pH 4.4) and

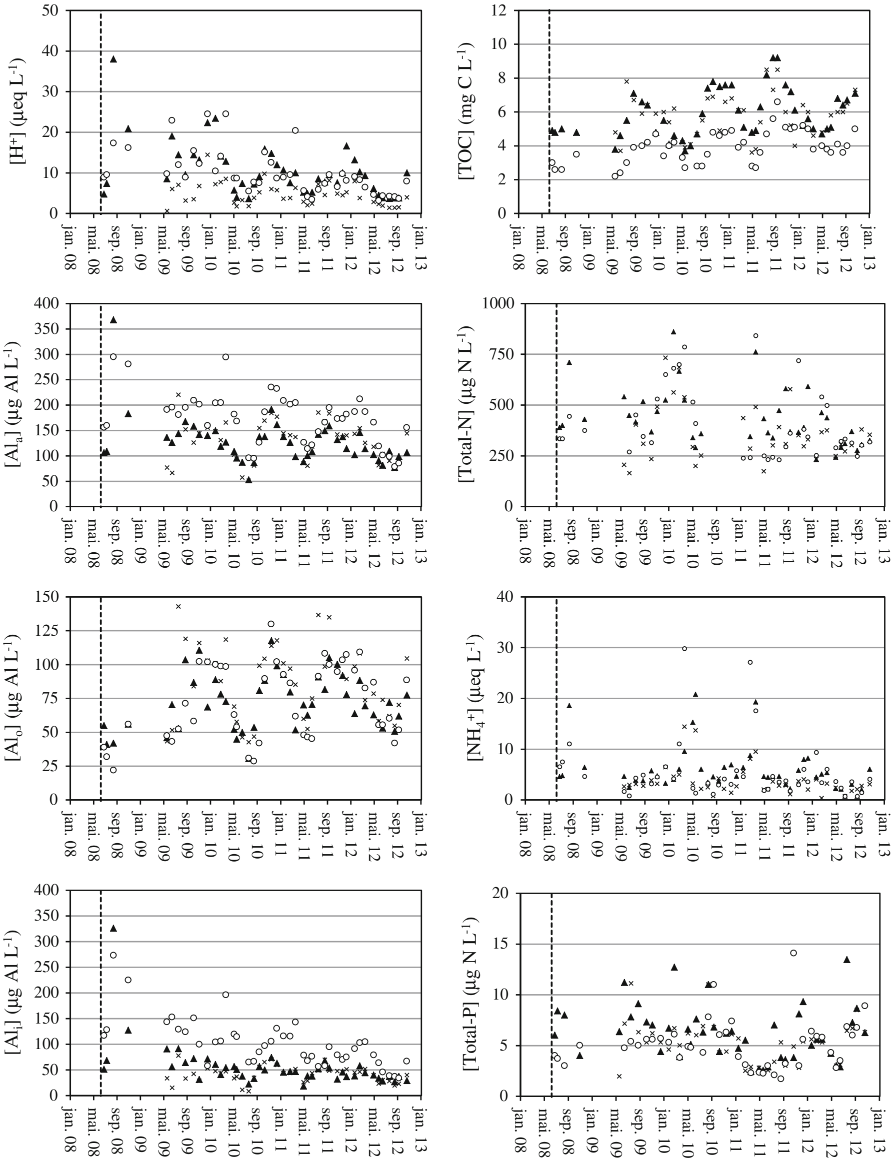


Fig. 4 Concentrations of H^+, TOC, Total-N, NH_4^+, Total-P and different Al fractions (Al_a, Al_o, Al_i) in Lake Hundsvatn *black upper triangle*, Lake Rasvassvatn *white circle*, and the control lake, Lake Jordtjenn *multi sign*, from June 2008 until October 2012. The monitoring started in the control lake in May 2009

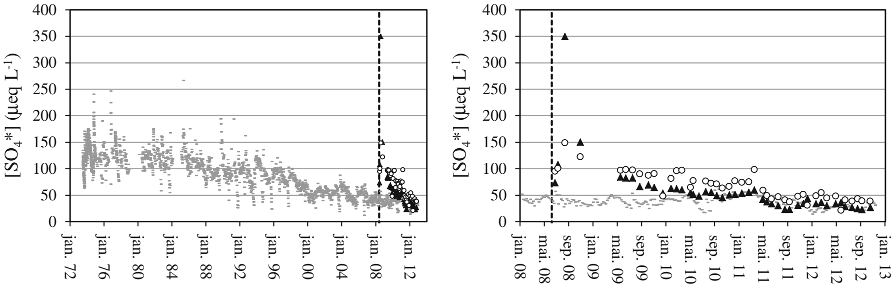


Fig. 5 Concentrations of non-marine sulfate (SO4*) in Lake Hundsvatn *black upper triangle*, Lake Rasvassvatn *white circle*, and at the nearby monitoring site, Birkenes *dash*. The *left panel* covers the period 1973 (January 1)–2012 (October 23), while the *right panel* covers the period from January 2008 until October 2012. *Dotted lines* indicates starts of the wild fire

326 μg Al_i L^{-1} (36 μeq L^{-1} as Al^{3+}) in Lake Hundsvatn. The H^+ concentration in Lake Rasvassvatn (17 μeq L^{-1}, pH 4.8), was very similar to the level at Birkenes, but the Al_i concentration was substantially higher in Lake Rasvassvatn, 273 μg Al L^{-1} (30 μeq L^{-1} as Al^{3+}). The concentrations of total monomeric aluminum (Al_a) were about equal at the three sites, i.e. 368, 295 and 310 μg Al L^{-1} in Lake Hundsvatn, Lake Rasvassvatn and Birkenes, respectively (Table 2).

Potassium (K^+) showed the strongest relative increase after the wildfire. The concentration in Lake Hundsvatn was 70 μeq L^{-1}, ≈70 times higher than Birkenes (Table 2). However, [K^+] had the lowest concentration of the four major base cations.

At the extreme water chemical conditions in August 2008, relatively low levels of both [NH_4^+], 11–19 μeq L^{-1}, and particularly [NO_3^-], 3–5 μeq L^{-1}, were observed in the wildfire affected lakes (Table 2). The concentrations of total phosphorous (Tot-P) in the lakes during the first post-fire year were relatively low, i.e. annual means of 7.6 ± 2.1 and 5.3 ± 0.4 μg P L^{-1} in Lake Hundsvatn and Lake Rasvassvatn, respectively. As the Regional Kendall test indicated significant decreases in Tot-P in the wildfire affected lakes (slope: −0.46 μg L^{-1} $year^{-1}$; $P = 0.004$) and not in the control lakes during the postfire period 2009–2012, we conclude that the wildfire probably caused a minor increase in Tot-P during the first post-fire year.

Similarly, as the Regional Kendall test indicated significant increases in TOC in wildfire affected lakes (slope: -0.23 mg C L^{-1} yr^{-1}; $p = 0.038$) and not in the control lakes during the post-fire period 2009–2012, we assume a decrease in TOC during the first post-fire year, perhaps a consequence of combustion of organic matter with subsequent reduced transport of allochthonous matter into the lakes.

Between the wildfire and start of the main monitoring on May 19, 2009, the lakes went through two turnovers (autumn 2008 and spring 2009) and one snowmelt period (spring 2009). During this period, the concentrations of ions have declined dramatically from the peak observed in August 2008. The electrolytic conductivity (K_{25}) declined by 67 % in Lake Hundsvatn, i.e. from 8.04 mS m^{-1} in August 2008 to 2.67 mS m^{-1} in May 2009. The corresponding decrease in Lake Rasvassvatn was 29 %, from 4.21 to 2.98 mS m^{-1}. The largest percentage decreases were shown by H^+, NH_4^+, Al_i and SO_4^{2-} (and SO_4*) in Lake Hundsvatn, all with decreases >70 % from August 2008 until May 2009. Only NO_3^- showed an increase in Lake Hundsvatn during the same time period, but the increase from 3 to 12 μeq L^{-1}, is of minor importance for the macro-chemistry in the lake.

As the decrease in [ΣBC*] in Lake Hundsvatn from August 2008 to May 2009, was much smaller (−177 μeq L^{-1}) compared with the decrease in [SO_4*], −265 μeq L^{-1}, a large increase in ANC occurred in this lake during this period, i.e. from −80 μeq L^{-1} in August 2008, to ≈0 μeq L^{-1} in May 2009.

The largest percentage decreases in Lake Rasvassvatn from August 2008 to May 2009, were observed for [NH_4^+] (−85 %), [Al_i] (−47 %) and [H^+] (−44 %), but the largest absolute decrease in equivalents was documented for [SO_4*], which decreased by 54 μeq L^{-1}, corresponding to a percentage decrease of 35 %. As in Lake Hundsvatn, the NO_3^- levels were generally low, and an increase was recorded from August 2008 to May 2009. The concentration of ΣBC* in Lake Rasvassvatn was slightly higher (7.1 %) in May 2009 compared with August 2008. As [SO_4*] decreased significantly during the same time interval, ANC increased from −39 μeq L^{-1} in August 2008 to 16 μeq L^{-1} in May 2009.

Long term trends in water chemistry of the wildfire affected lakes

The most severe water chemical conditions and the most significant water chemical recovery from the fire, occurred within the first post-fire year. In August 2012, >4 years after the fire, ΣBC* and SO_4* were reduced by 88 and 93 %, respectively in Lake Hundsvatn, and by 72 and 71 % in Lake Rasvassvatn compared with August 2008.

Based on the Regional Kendal test, no significant chemical trends were found in the control lakes during the period May 2009–October 2012, except for a significant decreases in [Ca^{2+}], [ΣBC*] and ANC, as a direct consequence of the unplanned liming of an inlet stream of Lake Svarttjenn in August 2009.

For the four wildfire affected lakes with the highest ANC values, Lake Øyvatn, Lake Grunnetjenn, Lake Hundsvatn and Lake Rasvassvatn, larger decreasing rates were calculated for [SO_4*] compared [ΣBC*] during the period May 2009–October 2012 (Table 5). For the remaining two lakes with the lowest ANC, Lake Fisketjenn and Lake Heitjenn, somewhat

Table 5 Calculated concentration (μeq L^{-1}) and half-life for non-marine base cations (ΣBC*) and non-marine SO_4* in the 6 wild fired affected lakes from May 2009 ($C_{t=0}$) to October 2012 $C_{t=end}$, assuming first order reaction kinetic decay patterns

Lake	Parameter	$C_{t=o}$ (μeq L^{-1})	$C_{t=end}$ (μeq L^{-1})	slope (k)	SE k	r^2	$t_{1/2}$ (days)	$t_{1/2}$ (years)
Heitjenn	BC*	100	17	−1.4E−03	1.8E−04	0.63	495	1.36
Heitjenn	SO4*	75	17	−1.2E−03	8.6E−05	0.84	590	1.62
Fisketjenn	BC*	98	27	−1.0E−03	1.8E−04	0.46	673	1.84
Fisketjenn	SO4*	71	24	−8.5E−04	9.5E−05	0.68	818	2.24
Grunnetjenn	BC*	153	49	−9.2E−04	1.0E−04	0.68	756	2.07
Grunnetjenn	SO4*	89	25	−1.0E−03	9.6E−05	0.76	679	1.86
Hundsvatn	BC*	109	44	−7.2E−04	9.4E−05	0.60	961	2.63
Hundsvatn	SO4*	78	25	−9.1E−04	7.0E−05	0.82	759	2.08
Rasvassvatn	BC*	112	48	−6.8E−04	9.3E−05	0.58	1017	2.79
Rasvassvatn	SO4*	101	35	−8.4E−04	9.2E−05	0.68	828	2.27
Øyvatn	BC*	152	97	−3.6E−04	7.6E−05	0.38	1936	5.30
Øyvatn	SO4*	72	36	−5.5E−04	1.0E−04	0.43	1270	3.48

k slope of the equations, *SE k* standard error of k. $P < 0.05$ for all regressions

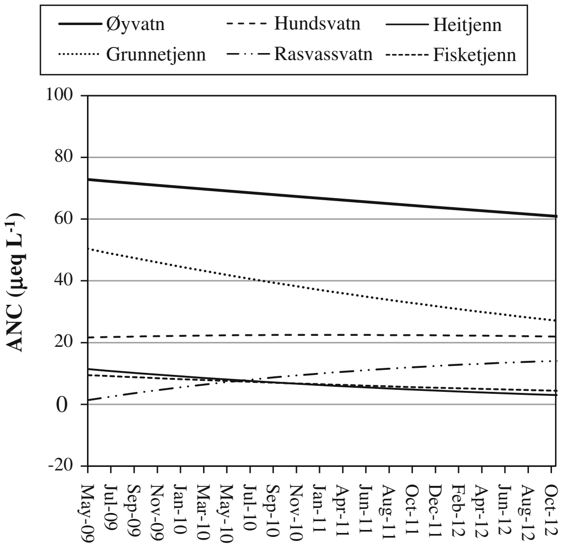


Fig. 6 Calculated trends in ANC in the wildfire impacted lakes from May 2009, one year after the wild fire, to October 2012, based on the decay constants of BC and SAA presented in Table 5. Only the trend in ANC of Lake Grunnetjenn is significant ($P = 0.045$)

stronger decreases were documented in [ΣBC*] compared with [SO_4*] during the same time period (Table 5). However, only Lake Grunnetjenn exhibited a significant ($P = 0.045$), change in ANC (decreasing trend) during period May 2009–October 2012 (Fig. 6).

Based on the Regional Kendal test, significant decreases in Tot-N (−53 µg N L^{-1} year^{-1}, $P = 0.008$) and NO_3^- (−2 µeq N L^{-1} year^{-1}, $P = 0.0001$) occurred from 2009 to 2012, while the decrease in NH_4^+ was not significant ($P = 0.071$). The highest post-fire concentrations of NH_4^+ and NO_3^-, did not occur during the extreme conditions in August 2008, but during later snow melt episodes. The highest concentrations of NH_4^+ came during snowmelt in 2010 and 2011 (Fig. 4), with concentrations of ≈20 µeq L^{-1} in Lake Hundsvatn and ≈30 µeq L^{-1} in Lake Rasvassvatn, while the highest NO_3^- concentrations came during the initial snow melt in Mars 2011, with concentrations of ≈35 and ≈25 µeq L^{-1} in Lake Rasvassvatn and Lake Hundsvatn, respectively (Fig. 3).

Discussion

Post-fire effects on water quality can be highly variable depending on factors such as hydrological regime, topography, geology, fire-size, fire-intensity, lake morphometry, the ratio of catchment to lake area, and water residence time (Ranalli 2004; Carignan et al. 2000). The relatively large differences in chemical response between lakes within the Mykland wildfire area, as well as large chemical variations in surface water responses of wildfires reported elsewhere (e.g. Smith et al. 2011), are primarily explained by these variables.

The wildfire in Mykland occurred in an area dominated by thin and patchy, base-poor and weathering resistant soils and bedrock. Thus, low ANC values in surface water are typical for this area. The long drought period ($\approx$1 month) followed by a 1 week-long wildfire, provided excellent conditions for sulfide oxidation within the catchments. Combined with the large mineralization of organic matter and killing of the vegetation, as direct effects of the wildfire, a substantial pool of inorganic cations and anions was ready to be mobilized from terrestrial to aquatic systems during the first rain events. However, the most extreme water chemical conditions did not occur during the first rain events, probably because the soil water first had to be replenished, and runoff was minor. This peak in water chemistry came at the end of a strong rain event, two months after the fire, and was likely the result of a strong flush of wildfire impacted water from the catchments to the lakes.

For the two wildfire affected lakes sampled during this extreme episode, Lake Hundsvatn and Lake Rasvassvatn, the most extreme chemical conditions were seen in Lake Hundsvatn, likely because of the high catchment-to-lake area ratio (17.6), compared with Lake Rasvassvatn (1.38). The significant delay in water chemical response after the fire and the variations in this delay, might be explained by factors such as post-fire hydrologic status of the catchments and lake residence times, factors which have received little attention in earlier studies of wildfire effects on surface waters. Ferreira et al. (2005) studied mechanisms driving hydrological and solute movement processes from terrestrial to aquatic systems as they change with time following forest fire, and Chessman (1986) reported time-variations in peak response of nitrate in various wildfire affected streams in south-eastern Australia.

As in our study, many articles have documented significant peaks in strong acid anions ([SAA]: SO_4^{2-}, Cl^- and NO_3^-) and base cations ([ΣBC]: Ca^{2+},Mg^{2+}, Na^+ and K^+) in lakes and streams during the initial post-fire period (Bayley et al. 1992b; Carignan et al. 2000; Eriksson et al. 2003; Mast and Clow 2008; Smith et al. 2011), but the peak concentrations and the relative increases compared with pre-fire values, particularly in Lake Hundsvatn (Table 2), are among the highest reported in the literature, especially [K^+] (peak: 70 μeq L$^{-1;}$ 70-fold increase) and [SO_4^{2-}] (peak: 367 μeq L^{-1}; 8.2-fold increase). This indicates a very intense wildfire, with significant mineralization of organic matter and killing of vegetation within this acid sensitive area, heavily impacted by acid deposition for decades (Schartau et al. 2012). Bayley et al. (1992b) reported a peak concentration of SO_4^{2-} (634 μeq L^{-1}) in a stream in Ontario, Canada, following a wildfire in 1980. The background concentration of SO_4^2 in this stream in 1980 was 59.7 μeq L^{-1}, which is about twice the background levels of that present in the lakes within the Mykland area in 2012. But the very high peak concentration of sulfate in the wildfire affected streams in Canada in 1980, might also be attributed in part to acid deposition. As a result of the significant declines in sulfur emissions in Europe since 1980, the SO4* concentration in southern Norway has declined by 70–80 % from 1980 to 2012 (Aas et al. 2012).

The concentration peaks in Na^+ and Cl^- ([Na^+] = 125 μeq L^{-1}, [Cl^-] = 165 μeq L^{-1}) in the wildfire affected lakes, were also relatively high compared with many other studies. Both background and post-fire peak concentrations of these ions are very dependent on the distance from the sea, the main source for these constituents. The far most extreme Na^+ and Cl^- conditions reported, are from wildfire affected streams in Tyresta, Sweden, August 1999 (Eriksson et al. 2000), but due to large amounts of brackish water used during the fire-fighting operations (Eriksson et al. 2003), their data are not directly comparable with most other wildfire impacted surface waters.

ANC in Lake Hundsvatn was 11 μeq L^{-1} on June 25, 9 days after the fire. By July 9, ANC had declined to −3 μeq L^{-1}, and then dropped to −80 μeq L^{-1} on August 13, during the 3rd post-fire rain event, 2 months after the fire. A decrease in ANC due to faster mobilization of strong acid anions (Cl^- and particularly SO_4^{2-}) compared with base cations during the initial post-fire period, has earlier been described in base-poor boreal forest streams in Ontario, Canada (Bayley et al. 1992b). They reported a mean annual ANC decrease of 20 % compared with the mean ANC value of the last pre-fire year, but the annual mean ANC value was still positive. However, even though not commented on in their study, we assume that a severe decline in ANC must have occurred during the extreme peak in SO_4^{2-} (634 μeq L^{-1}) reported soon after the wildfire.

After the initial post-fire period, [SO_4*] decreased faster than [ΣBC*] in Lake Hundsvatn water the

Table 6 Calculated concentration decreases (µeq L^{-1}) in non-marine base cations (BC*) and non-marine sulfate (SO_4*) from August 2008 to August 2009 ($n = 6$), and from 2009 to August 2012 in Lake Hundsvatn, showing different first order reaction decays for the two periods, $C_{t=0}$ and $C_{t=end}$ is the measured concentrations at the start and the end of the calculated periods

Period		$C_{t=o}$	$C_{t=end}$	k	SE k	r^2	p	$t_{1/2}$ (days)	$t_{1/2}$ (years)
Aug08–Aug09	BC*	272	103	−2.21E−03	5.02E−04	0.83	0.012	314	0.86
	SO_4*	350	66	−3.87E−03	6.06E−04	0.91	0.003	179	0.49
Aug09–Aug12	BC*	103	32	−7.36E−04	1.22E−04	0.52	0.000	942	2.58
	SO_4*	66	25	−8.62E−04	8.90E−05	0.73	0.000	804	2.20

k slope of the equations, *SE k* standard error of k

following months. Theoretically, assuming first order decay patterns (Table 6), [ΣBC*] was equal to [SO_4*] in Lake Hundsvatn, i.e. ANC = 0, 150 days (≈5 months) after the severe drop in ANC in August 2008. This means that predominantly positive ANC values were re-established in Lake Hundsvatn five months after the extreme water chemical peak, seven months after the fire. In May 2009, almost one year after the wildfire, ANC was back to almost pre-fire values, i.e. ANC ≈ 20 µeq L^{-1} (Fig. 6).

From May 2009 to October 2012, the concentrations of [SO_4*] decreased faster than [BC*] in four of the six wildfire affected lakes, but without any significant increase in ANC in five of the lakes. Only Lake Grunnetjenn showed a significant declining trend ($P = 0.045$) in ANC during this period. In the two lakes with lowest ANC, Lake Fisketjenn and Lake Heitjenn, the concentration of ΣBC* declined somewhat faster than [SO_4*] (Table 5), but in neither of these lakes significant ANC trends were observed from May 2009 to October 2012 (Fig. 6). The most reasonable explanations for no significant ANC changes in lakes after the first post-fire year, are likely an interplay between several factors that decrease ANC as:

- Faster decrease in [ΣBC*] in surface water compared with [SO_4*], after the chemical post-fire peak, as recorded in two of the wildfire affected lakes, implies a gradual ANC decrease by time.
- Significant decrease in ionic strength in surface water after a wildfire, implies a pure dilution effect, which *per se* implies a decrease in ANC by time when the ANC is positive.

and factors that increase ANC as:

- Faster decrease in [SO_4*] in surface water compared with [ΣBC*], after the chemical post-fire peak, as recorded in 4 of the wildfire affected lakes, implies a gradual ANC increase by time.
- Significant decrease in ionic strength in surface water after a wildfire, implies a pure dilution effect, which *per se* implies an increase in ANC by time when the ANC is negative.
- The significant increase in TOC observed in the wildfire effected lakes (Table 6) after the first post-fire year, should gradually lead to an ANC increase by time, due to increased concentration of weak organic acids and the fact that increase in TOC also implies increase in base cations and subsequent increase in ANC (Lydersen et al. 2004).

In addition, the relative trends in [Cl^-] and [Na*] affect trends in ANC.

Despite very low pH and high concentrations of Al_i, the toxic, inorganic, cationic forms of Al (Schofield 1977; Dickson 1978) during the extreme event in August 2008, the concentrations of total monomeric aluminum (Al_a) were very similar in Lake Hundsvatn, Lake Rasvassvatn and Birkenes, i.e. 368, 295 and 310 µg Al L^{-1} (Table 2). The most likely reason for the much higher Al_i in the wildfire affected lakes compared with Birkenes, is a combination of decrease in organic matter and a substantial increase in sulfuric acid (pH decrease) as direct effects of oxidation of organic and inorganic compounds within the wildfire area.

Little data exists on pH, ANC and aluminum in surface water after wildfires. In the Tyresta wildfire in Sweden, where brackish water was used during the fire-fighting, one of the least affected streams, showed a pH decrease to pH 4.5 and an Al_i increase to 330 µg Al L^{-1} (Eriksson et al. 2003), conditions very similar to the levels observed during the post-fire peak in Lake Hundsvatn 2008. The extreme low pH and ANC and the very high concentrations of Al_i measured in Lake Hundsvatn (pH: 4.42; ANC: −80 μeq L^{-1}; Al_i: 326 μg Al L^{-1}) and Lake Rasvassvatn (pH: 4.76; ANC: −39 μeq L^{-1}; Al_i: 273 μg Al L^{-1}) should be lethal for fish species such as perch and brown trout (Lydersen et al. 2002, 2004), fish species present within the wildfire area. However, no significant fish death has been reported. There might be several reasons for this. Lack of documentation as very few people were in the area at that time, the extreme water chemical episode was too short to have substantial lethal impact and/or fish might have migrated down into the marginal wildfire affected hypolimnion water, as both lakes were temperature stratified at that time of the year.

Large post-fire variations in export of N and P from different forest environments to aquatic systems, are reported in the literature (Smith et al. 2011). In our study, increases in NO_3^-, $NH_4^+$and total N were seen during the first extreme water chemical peak in August 2008, but the concentrations were still relatively low. The low initial post-fire increases in N-compounds, followed by higher levels of these compounds during winter and snowmelt in the first post-fire years in our study, are also reported in other wildfire studies (Bayley et al. 1992b; Carignan et al. 2000; Mast and Clow 2008). One exception is the lack of effects of NH_4^+ in streams after the wildfire in Glacier National Park, Montana, reported by Mast and Clow (2008). As there are no comparable pre-fire values of total phosphorous (Tot-P), we cannot quantify the immediate wildfire effects, but the concentrations of Tot-P in the lakes during the first post-fire year were relatively low. Most wildfire studies document an increase in Tot-P during the initial post-fire period, followed by a gradual decrease again back to pre-fired levels during a few years (Ranalli 2004).

The fact that nitrate concentrations remained elevated in winter, especially related to snowmelt episodes during the three first post-fire winters, and fell back to pre-fire concentrations in the growing season, two years after the wildfire, are time patterns very similar to that observed by Mast and Clow (2008). Thus, two years after the wildfire, the N-uptake by vegetation has increased sufficiently to return concentrations to near background levels during the growing season.

The moderate concentration increases in NO_3^- and NH_4^+ observed after wildfire in Mykland, agree well with earlier studies of wildfire affected streams in base-poor boreal forest systems in Ontario, Canada (Bayley et al. 1992b) and in northern subalpine rocky mountains areas in Montana, USA (Mast and Clow 2008), and in wildfire affected lakes from boreal subarctic areas in northern Alberta (McEachern et al. 2000). There might be several causes for only moderate increases of nitrogen compounds in wildfire impacted surface waters:

- Very good oxidation conditions during the wildfire imply large amounts of NO_x emissions to the atmosphere and subsequent large transport of NO_x gases out of the catchments.
- Boreal forests are nutrient poor environments particularly low in N (Foster and Morrison 1976; Gosz 1981).
- Soils are too shallow to allow nutrients to leach below the rooting zone. Accordingly, most of the nutrients are probably retained by the new vegetation (Bayley et al. 1992b)

Regarding TOC, there are no comparable pre-fire data for evaluation of immediate effects of wildfire, but the significant increase in TOC observed from May 2009 to October 2012, indicates an initial TOC decrease, which might be directly related to combustion of organic matter during wildfire, and the subsequent increase in TOC the following years as new vegetation is gradually re-established in the area. Similar post-fire trends in TOC in surface water have also been documented in other studies (McEachern et al. 2000; Carignan et al. 2000).

Conclusion

The wildfire in Mykland occurred in an area basically consisting of thin and patchy, base-poor soils and slowly weatherable rocks.

The most severe chemical conditions in wildfire affected surface waters occurred during some of the first post-fire rain events, but the amount of rain in relation to the hydrological status of the catchment prior to these events, and lake residence time, are decisive factors regarding when the most extreme water chemical conditions arise in surface waters affected by wildfire.

During the first post-fire hydrological episodes, strong acid anions as Cl^- but primarily SO_4^{2-}, are mobilized significantly faster from terrestrial to aquatic systems compared with base cations (ΣBC), which means that the acid neutralizing capacity (ANC: [ΣBC]–[SAA]) of lakes decline. For lakes with low pre-fire ANC values, significant drops in ANC down to very low negative values might occur, with subsequent increase in $[H^+]$ and toxic inorganic Al $[Al_i]$ to levels potentially harmful to aquatic life. In lakes with higher pre-fire ANC values, the drop in ANC during the first post-fire period is too small to cause severe acidification, and therefore harmless to aquatic life. Normal ANC values seem to be reestablished relatively fast in wildfire affected lakes, often within the first post-fire year.

After the extreme, post-fire water chemical peak, the main mobile anions (Cl^- and SO_4^{2-}) decreased faster than ΣBC. This combined with increase in TOC should imply a potential increase in ANC with time after fire in wildfire affected lakes. However, at the same time, the continuous dilution effect back to pre-fire levels, might counteract this potential ANC increase. This might explain why no ANC increase was seen in five of the six wildfire affected lakes, from one year after the fire and the next three post-fire years.

Increases in nutrients, N and P, and decreases in TOC in surface water during the initial post-fire period, followed by a gradual decrease in N and P and increase in TOC during the next post-fire years, have also been seen in surface waters from other wildfire impacted areas.

The water chemistry in the wildfire affected lakes in the Mykland area, had almost returned to pre-fire conditions 4.5 years after the wildfire. Thus, in this area of Norway, with significant reductions in acid deposition during the last decades, with $[SO_4^*]$ reduction by 75–88 % in lakes from 1980 to 2011 (Schartau 2012), the most severe water chemical episodes, are again primarily driven by sea-salt events, directly linked to hydrologic episodes, directly as a result of heavy rain, or indirectly during snow melt as the sea-salt episode(s) are "accumulated" in the snowpack.

Hydrological regime, topography, geology, fire intensity, fraction of catchment burnt, lake morphometric conditions such as catchment-to-lake area ratio and lake residence time, are key factors for the variations in water chemical response in wildfire affected lakes.

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