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 ($[\Sigma BC]$) 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 $-80\ \mu eq\ L^{-1}$, while $[H^+]$ and inorganic aluminum ($[Al_i]$) increased to 38 $\mu eq\ L^{-1}$ (pH 4.42) and 326 $\mu g\ Al\ L^{-1}$ (36.2 $\mu eq\ L^{-1}$ 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 $[\Sigma BC]$, 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 $[\Sigma BC]$ 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.

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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

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)
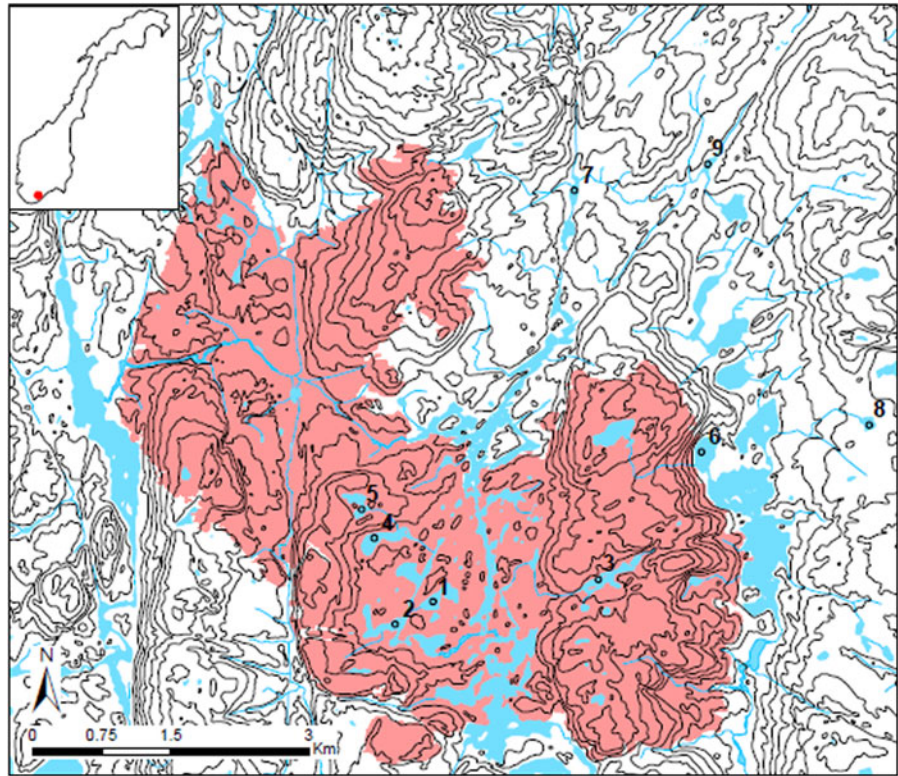

Table 1 Median water chemistry in the control lakes in 2009 and 2012

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^+	$\mu eq\ L^{-1}$	6.0	2.6	3.2	4.6	3.9	5.1
Ca^{2+}	$\mu eq\ L^{-1}$	47	42	73	46	59	62
Mg^{2+}	$\mu eq\ L^{-1}$	25	28	26	27	26	29
Na^+	$\mu eq\ L^{-1}$	76	65	69	65	93	122
K^+	$\mu eq\ L^{-1}$	9.5	6.9	9.0	5.9	2.8	5.9
$NH_4^+–N$	$\mu eq\ L^{-1}$	3.2	2.3	3.9	2.3	6.9	3.3
SO_4^{2-}	$\mu eq\ L^{-1}$	43	39	35	32	15	30
Cl^-	$\mu eq\ L^{-1}$	66	72	65	69	99	141
$NO_3^-–N$	$\mu eq\ L^{-1}$	2.2	1.4	2.6	1.1	3.7	1.9
SO4*	$\mu eq\ L^{-1}$	35	31	27	26	5.0	16
ΣBC*	$\mu eq\ L^{-1}$	85	67	102	62	80	68
TOC	$mg\ C\ L^{-1}$	5.9	6.0	7.1	7.4	7.4	9.9
ANC	$\mu eq\ L^{-1}$	49	29	74	33	67	51
Total-N	$\mu g\ N\ L^{-1}$	309	305	298	356	488	460
Al_a	$\mu g\ Al\ L^{-1}$	145	111	122	143	120	170
Al_o	$\mu g\ Al\ L^{-1}$	103	74	95	108	102	127
Al_i	$\mu g\ Al\ L^{-1}$	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
Altitute 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	%	≈100	≈100	≈100	≈100	≈100	≈90	0.0	0.0	0.0

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:

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

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

$$[ANC]: \Sigma \left[Ca^{2+}\right], \left[Mg^{2+}\right], \left[Na^{+}\right], \left[K^{+}\right] - \Sigma \left[SO_4^{2-}\right],$$
$$\left[NO_3^{-}\right], \left[Cl^{-}\right])$$

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):

$$SO_4^* = \left[SO_4^{2-}\right] - 0.103[Cl^-];$$
$$Ca^* = \left[Ca^{2+}\right] - 0.037[Cl^-];$$
$$Mg^* = \left[Mg^{2+}\right] - 0.195[Cl^-];$$
$$Na^* = \left[Na^{+}\right] - 0.859[Cl^-];$$
$$K^* = \left[K^{+}\right] - 0.0181[Cl^-]$$

As the macro-chemical effects of wildfire on surface waters, basically deals with the relationship between effects of strong acids (basically SO_4^*) 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
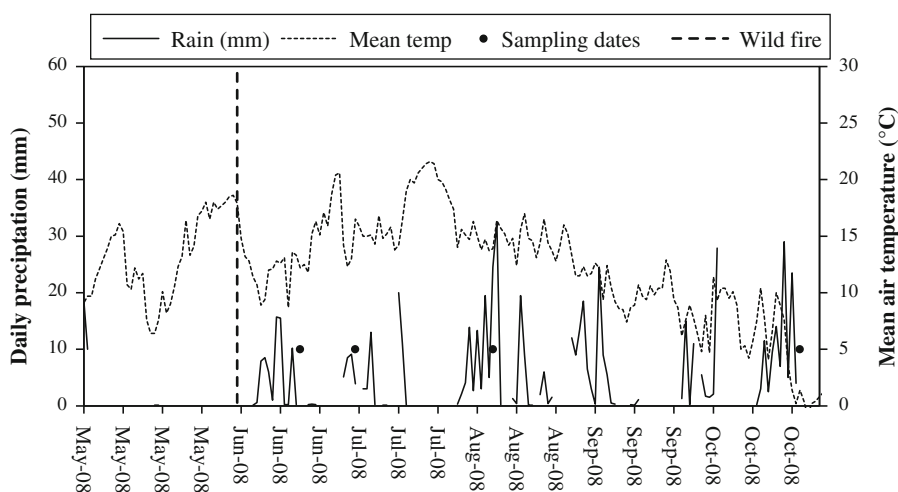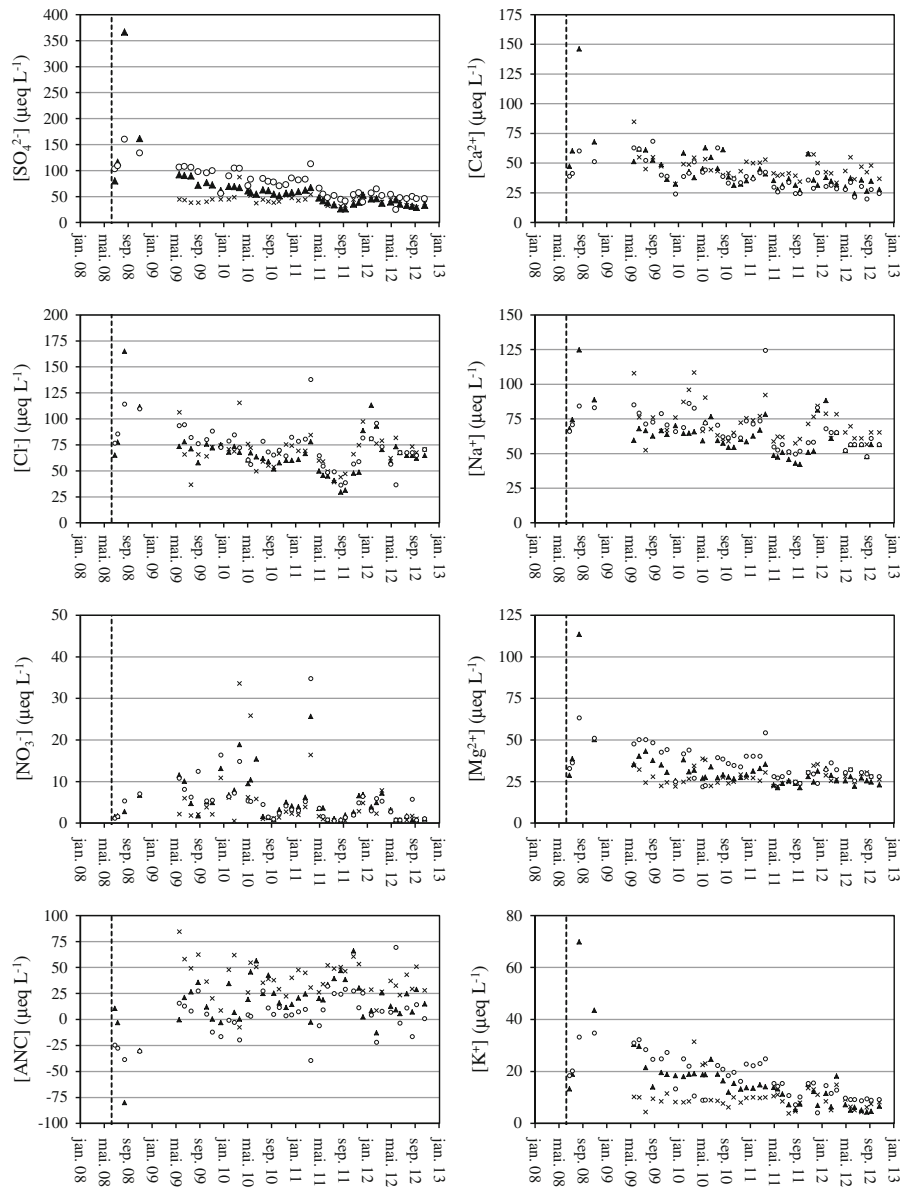
Fig. 3 Concentrations of strong acid anions, base cations and ANC in Lake Hundsvatn *black upper triangle*, Lake Rasvassvatn *white circle*, and the control lake, Lake Jordtjenn *multi sign*, from June 2008 until October 2012. The monitoring started in the control lake in May 2009

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, NH4+, Total-P and different Al fractions (Ala, Alo, Ali) 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
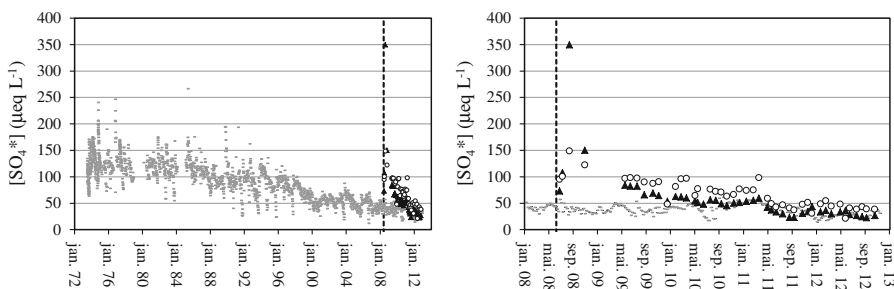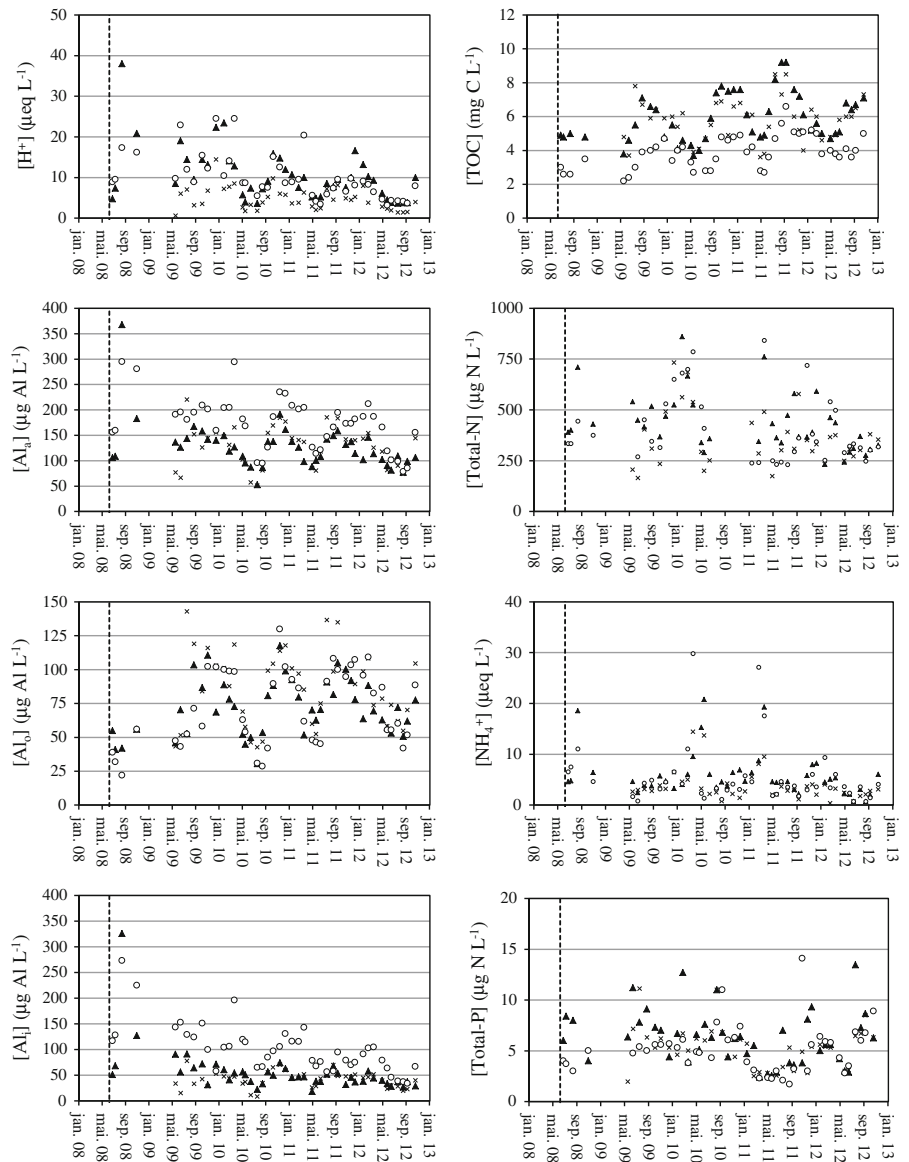
Fig. 5 Concentrations of non-marine sulfate (SO4*) in Lake Hundsvatn *black upper triangle*, Lake Rasvassvatn *white circle*, and at the nearby monitoring site, Birkenes *dash*. The *left panel* covers the period 1973 (January 1)–2012 (October 23), while the *right panel* covers the period from January 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
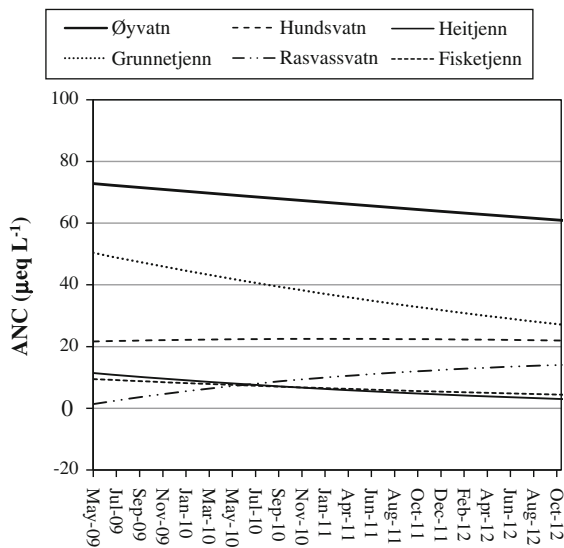

Fig. 6 Calculated trends in ANC in the wildfire impacted lakes from May 2009, one year after the wild fire, to October 2012, based on the decay constants of BC and SAA presented in Table 5. Only the trend in ANC of Lake Grunnetjenn is significant (*P* = 0.045)

$P = 0.008$) 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 snow-melt 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.

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},

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 (≈ 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 southeastern 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, [SO4*] 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 <u>declining</u> 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 <u>when</u> 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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