

# Amines in surface waters: A survey of Norwegian lakes



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**Abstract**

Amine-based CO<sub>2</sub> capture is one of the most promising technologies for emissions reductions from stack gases. In the summer of 2012, we measured the concentrations of amines in 21 Norwegian lakes with the aim of assessing the prevalence of amines in Norwegian lakes and identifying the main factors affecting concentrations of these compounds. Dimethylamine (DMA) was the most prevalent amine (2 869–22 247 ng/L). Methylamine (MA) and monoethanolamine (MEA) concentrations were also high, ranging from 328–4 946 ng/L and 686–4 435 ng/L respectively. Intermediate concentrations were observed for piperazine (PIP; 454–842 ng/L) and diethylamine (DEA; <50–960 ng/L), while ethylamine (EA) and 2-amino-2-methyl-propanol (AMP) were not detected in any of the lakes. MEA concentrations were highest in eutrophic lakes and were most closely related to phytoplankton biomass (as indicated by chlorophyll *a*), suggesting that in lake production of MEA by primary producers may be an important source of this compound. Meanwhile, MA and DMA concentrations were highest in humic lakes (high TOC and low pH) where high terrestrial inputs of organic matter may be an important source of these amines. The high natural levels of several amines in Norwegian lakes have important implications for assessing the potential influence of emissions from amine-based CO<sub>2</sub> capture facilities.

|                           |                            |
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| 1. CO <sub>2</sub> fangst | 1. CO <sub>2</sub> capture |
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# **Amines in surface waters: A survey of Norwegian lakes**

## **Preface**

This survey of amine concentrations in Norwegian lakes was carried out by NIVA (Norwegian Institute for Water Research). The personnel involved in the project are outlined in Appendix 8.2, and are thanked for their important contributions to this study.

This study was performed on commission from Statoil, and we thank our contacts at Statoil for their support and input throughout the project. Analysis of amines was carried out at NILU (Norwegian Institute for Air Research) and we thank Christian Dye for his cooperation on the analytical work.

Oslo, December 2012

*Amanda Poste*

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## Summary

Amine-based CO<sub>2</sub> capture is one of the most promising technologies for emissions reductions from stack gases from fossil-fuel power plant and other industrial waste gases. Amine-based technology will be tested in Norway at Test Centre Mongstad (TCM). In 2011, prior to start-up of TCM, NIVA carried out a baseline survey of concentrations of several amines in lakes in the Mongstad region (Grung et al. 2011). Several of the lakes had relatively high concentrations of several amines. Globally there are few data available regarding concentrations of amines in natural surface waters.

Amines are widespread in the environment and have many natural as well as industrial sources. Organisms can produce and release amines to the environment, and many precursors to amines (including amino acids) are released by aquatic organisms either while alive, or during decomposition of deceased plants and animals. Other potential natural sources of amines (and amine precursors) to freshwaters include runoff from the terrestrial environment as well as sea birds and other migratory wildlife.

In summer 2012 we carried out a survey of amine concentrations in 21 Norwegian lakes with the aim of the prevalence of amines in Norwegian lakes and identifying the main factors affecting concentrations of these compounds. The lakes were chosen to cover a range of lake types, water chemistry, catchment land use, and influence of anthropogenic pollution. Samples were collected from the lake outlets. Water samples for amine determination were delivered to the Norwegian Institute for Air Research (NILU) within 48 hours of collection, derivatized, and then detected by reversed phase liquid chromatography coupled with mass spectrometry. Seven amines were determined (methylamine: MA; ethylamine: EA; dimethylamine: DMA; diethylamine: DEA; monoethanolamine: MEA; 2-amino-2-methyl-propanol: AMP; and piperazine: PIP). Detection limits for these amines ranged from 10–100 ng/L. Water samples were also delivered to the NIVA laboratory for determination of several water chemistry parameters, including: TOC, pH, TP, TN, SO<sub>4</sub>, NO<sub>3</sub>, Cl and Na, as well as chlorophyll *a* (as a measure of phytoplankton biomass).

As intended, the sites chosen covered a wide range in major component water chemistry and spanned gradients in the influence of several natural and anthropogenic drivers, including eutrophication, prevalence of wetlands in the catchment, and acidification.

Results from analysis of tap and MilliQ water revealed significant concentrations of several amines, even in these “blanks”. This may be a methodological artefact or may reflect that these waters do in fact contain amines. In a methodological artefact, these values should be treated as blanks and subtracted from measured concentrations in lake samples. Meanwhile, if these values represent amine contamination of tap and MilliQ water, these values should be treated as “reference” samples with low levels of amines, and not subtracted. We are working with NILU on additional tests to resolve this issue. We chose here to treat these values as “references” rather than true “blanks”.

As for the 10 lakes included in the 2011 Mongstad study, the most prevalent amine measured in water from the 21 lakes sampled in 2012 was DMA (2 869–22 247 ng/L). MA and MEA concentrations were also high, ranging from 327–4 946 ng/L and 686–4 435 ng/L respectively. Intermediate concentrations were observed for PIP (454–842 ng/L) and DEA (<50–960 ng/L), while EA and AMP were not detected in any of the lakes. Although amine concentrations have rarely been reported for lakes, these values are high relative to other observations for river water, and DMA concentrations observed those that have been reported for municipal wastewater.

MEA concentrations were highest in eutrophic lakes and were most closely related to phytoplankton biomass (as indicated by chlorophyll *a*), suggesting that in lake production of MEA by primary producers may be an important source of this compound. Meanwhile, MA and DMA concentrations were highest in humic lakes (high TOC and low pH) where high terrestrial inputs of organic matter may be an important source of these amines. These relationships hold regardless of whether or not reference (tap and MilliQ water) values were subtracted from lake concentrations.

Future work should entail resolving analytical uncertainty, and determining seasonal changes in concentrations of amines in surface waters. The high natural levels of several amines in Norwegian lakes have important implications for assessing the potential influence of emissions from amine-based CO<sub>2</sub> capture facilities.

## Norsk sammendrag

Aminbasert CO<sub>2</sub>-fangst er en av de ledende teknikkene for å redusere utslipp av denne klimagassen fra industrielle avgasser, både fra kullfyrte og oljefyrte energikilder. I Norge skal aminbasert teknologi testes ved Test Centre Mongstad (TCM). I 2011, før oppstarten av TCM, var NIVA ansvarlig for å gjennomføre en tilstandsundersøkelse som blant annet inneholdt en kartlegging av aminkonsentrasjoner i innsjøer i nærheten av Mongstad (Grung et al. 2011). Flere av de undersøkte innsjøene hadde relativt høye konsentrasjoner av noen av de undersøkte aminene. Det er få data tilgjengelig når det gjelder hvilke nivåer som er vanlig av aminer i naturlig overflatevann.

Aminer finnes overalt i miljøet, og har ulike naturlige så vel som industrielle kilder. Organismer kan produsere og avgi aminer til miljøet. Mange forløpere til aminer (bl.a. aminosyrer) stammer fra akvatiske organismer, enten mens de er i live, eller ved nedbrytning av plantemateriale eller døde organismer. Andre naturlige kilder til aminer i ferskvann er tilsig fra terrestrisk miljø, samt avføring fra fugler eller dyr.

Sommeren 2012 gjennomførte vi en undersøkelse av aminkonsentrasjoner i 21 norske innsjøer. Målet var å finne ut hvilke nivåer av aminer som var vanlige, samt å identifisere hvilke faktorer som bidro til de observerte nivåene. Innsjøene ble valgt for å omfattede ulike typer innsjøer, blant annet når det gjelder vannkemi, arealbruk i nedbørsfeltet og grad av menneskelig påvirkning. Vannprøver ble samlet fra utløpet av innsjøen. Vannprøver til bestemmelse av aminer ble levert til Norsk institutt for luftforskning (NILU) senest 48 timer etter prøvetakning. Etter mottak ble prøvene derivatisert, og aminer ble målt ved hjelp av reversert fase væskechromatografi koblet til et massespektrometer. Syv aminer ble bestemt: metylamin (MA), etylamin (EA), dimetylammin (DMA), dietylammin (DEA), monoetanolamin (MEA), 2-amino-2-metylpropanol (AMP) og piperazin (PIP). Deteksjonsgrensene varierte fra 10-100 ng/L. Vannprøver ble også levert til NIVAs laboratorium for bestemmelse av ulike kjemiske vannparametre: totalt organisk karbon (TOC), pH, totalt fosfor (TP), totalt nitrogen (TN), ammonium (SO<sub>4</sub>), nitrat (NO<sub>3</sub>), Cl, og klorofyll *a* (som et mål på biomassen av planktonalger).

Analysen av vannkjemien viste at vi hadde lyktes i å velge innsjøer med et bredt spekter av de parameterne vi analyserte, både når det gjelder naturlige og menneskelig påvirkning. Dette inkluderer eutrofiering, graden av myrområder i nedbørsfeltet og forsuring.

Analysene av aminer i springvann og MilliQ-vann viste høye nivåer av flere aminer, selv i prøver som kan anses som «blanke». Dette kan være en metodisk artefakt, eller kan også bety at vannet faktisk inneholder høye nivåer av aminer. Dersom dette er metodisk artefakt, skal disse verdiene behandles som blankprøver og derfor trekkes fra de målte konsentrasjonene i innsjøene. Dersom de forhøyede aminnivåene i kranvann og MilliQ-vann er reelle, bør disse nivåene behandles som referansenivåer. Vi samarbeider tett med NILU for å løse denne problemstillingen. I dette prosjektet har vi valgt å behandle disse verdiene som referanseverdier, og ikke som blankprøver.

I likhet med tilstandsundersøkelsen rundt Mongstad i 2011, inneholdt innsjøene vi undersøkte i 2012 høye nivåer av DMA (2 869-22 247 ng/L). Konsentrasjonene av MA og MEA var også høye: 327-4 946 og 686-4 465 ng/L. Lavere nivåer ble målt for PIP (454-842 ng/L) og DEA (<50-960 ng/L). EA og AMP ble ikke påvist over deteksjonsgrensen i noen av innsjøene. Selv om aminnivåer sjelden har blitt rapportert i innsjøer, er disse verdiene høye sammenlignet med de få andre undersøkelsene som finnes av nivået i elver. Det nivået som vi finner av DMA er sammenlignbart med det som er rapporter for kommunalt avløpsvann i andre undersøkelser.



Våre undersøkelser viser at MEA-nivået var høyest i eutrofe innsjøer, og var korrelert med biomassen til planktonalger (representert ved analyse av klorofyll *a*). Dette tyder på at MEA i innsjøen stammer fra primærprodusenter som antagelig representerer en viktig kilde til denne komponenten. På den annen side observerte vi høye konsentrasjoner av MA og DMA i humusrike innsjøer (høyt innhold av TOC og lav pH) der tilsig av organisk materiale fra jord/myr kan være en viktig kilde til disse aminene. Disse sammenhengene er uavhengig av om vi behandler springvann og MilliQ-vann som referanseprøver eller som blankprøver.

Fremtidig arbeid bør avklare de analytiske usikkerhetene, og bør også avklare om det finnes sesongvariasjoner i amin-nivåene. Det naturlig høye nivået av aminer i norske innsjøer har betydning for hvordan et forhøyet utslipp av aminer fra CO<sub>2</sub>-fangstanlegg vil påvirke det akvatiske miljøet.

# 1. Introduction

Technologies designed to capture and store CO<sub>2</sub> from combustion flue gases (post combustion capture: PCC) are increasingly being considered for use in reducing CO<sub>2</sub> emissions, particularly at sites where electricity is being produced using fossil fuels. Aqueous amines are the most common solvents for PCC and have long been used as solvents in CO<sub>2</sub> removal (“sweetening”) processes for natural gas (Reynolds et al. 2012). PCC activities are known to result in a loss of amines from the absorber column, and as such, may represent a potential source of amines and amine degradation products (including nitrosamines and nitramines) to the environment (Reynolds et al. 2012), which is of concern with respect to potential toxic effects on aquatic ecosystems (Veltman et al. 2010).

CO<sub>2</sub> capture and storage has been proposed for Norwegian gas-fired power plants (Kårstø and Mongstad) as a means of reducing CO<sub>2</sub> emissions to the atmosphere, and amine-based PCC technology will be tested in Norway at Test Centre Mongstad (TCM). In 2011, in conjunction with TCM and the Norwegian Institute for Forest and Landscape (Skog og Landskap), NIVA carried out a baseline survey of concentrations of several amines in the Mongstad region (Grung et al. 2011).

Amines are widespread in the environment and have many natural as well as industrial sources. Biogenic amines can be formed through decarboxylation of amino acids (often through microbial processes), or by amination of ketones and aldehydes (Santos 1996). In the aquatic environment, many aquatic organisms are capable of producing and releasing amines (both primary amines as well as more complex compounds) to the surrounding environment. In the aquatic environment, studies in marine systems have indicated that aliphatic amines (such as methylamine, dimethylamine and diethylamine) often originate from biological sources (Facchini et al. 2008, Müller et al. 2009). Furthermore, many precursors to amines (including amino acids) are released by aquatic organisms while they are alive, or during decomposition of deceased plants and animals. These processes are likely to represent an important *in situ* source of amines to aquatic ecosystems.

Amines and amine precursors may also be delivered to freshwaters from their terrestrial catchments (while catchment export of both nitrate and nitrite may be of important in determining the potential for formation of nitrosamines and nitramines). Other potential natural sources of amines (and amine precursors) to freshwaters include sea birds and other migratory wildlife. These organisms could deliver amine and amine-related compounds to aquatic ecosystems through their faeces and urine both directly in the water and in the catchment. Furthermore, these organisms may be sources of both nitrates and nitrites, which may be of importance with respect to nitrosamine and nitramine formation.

There is a remarkably broad and complex range of potential sources of amines to the aquatic environment, including both natural as well as anthropogenic sources. This suggests that, in order to identify the potential for changes in delivery of these compounds (e.g. through amine-based CO<sub>2</sub> capture activities) and the resultant implications for aquatic ecosystem and human health, there is a strong need to identify the sources that are most prevalent and most important to determining eventual concentrations of these compounds in freshwaters. Also, results from the 2011 baseline survey in the Mongstad region (carried out by NIVA), suggest that for several amines, the concentrations observed are particularly high relative to those reported in other studies. This highlights a need for an assessment of the environmental factors related to amine concentrations in these lakes.

This survey of amine concentrations in Norwegian lakes was designed to meet the following objectives:

1. To characterize amine concentrations in a diverse set of lakes, in order to gain insight into the range of concentrations encountered in Norwegian lakes. Lakes were selected to achieve gradients in water chemistry, the relative influence of various human activities, and other factors.
2. To identify potential determinants of amine concentrations in Norwegian freshwaters.

## 2. Materials and methods

### 2.1 Study Sites

We selected a set of 21 study lakes across southern Norway (Table 1, Figure 1) and one seawater site, which was included as a marine reference. The study lakes were chosen to represent the range of conditions that exist in southern Norwegian lakes. Many of the lakes included in the current study have been a part of monitoring programs at NIVA for many years (often decades), and as such, for several of the study lakes there are many existing data that can be used to contextualize the results of the current study. Three of the lakes included in the current study were also included in the 2011 baseline study carried out in the Mongstad region (Fonnebostvatnet (A7; M11 in 2011 study), Langevatnet (A8; M16 in 2011 study) and Storavatnet (A9; M52 in 2011 study)), which will allow for temporal comparison of results.

**Table 1.** General characteristics of study lakes.

| Site Code | Lake            | County           | Area (km <sup>2</sup> ) | Elevation (m a.s.l.) | Latitude (°) | Longitude (°) | NVEnr |
|-----------|-----------------|------------------|-------------------------|----------------------|--------------|---------------|-------|
| A1        | Spiradammen     | Akershus         | 0.03                    | 13                   | 59.84        | 10.50         | 80670 |
| A2        | Lille Hovvatnet | Aust-Agder       | 0.22                    | 503                  | 58.61        | 8.04          | 10069 |
| A3        | Langtjern       | Buskerud         | 0.23                    | 516                  | 60.37        | 9.73          | 7272  |
| A4        | Steinsfjorden   | Buskerud         | 13.81                   | 63                   | 60.08        | 10.32         | 67985 |
| A5        | Atnsjøen        | Hedmark          | 5.01                    | 701                  | 61.89        | 10.14         | 126   |
| A6        | Mjøsa           | Hedmark          | 369.0                   | 123                  | 60.90        | 10.69         | 118   |
| A7        | Fonnebostvatnet | Hordaland        | 0.06                    | 23                   | 60.75        | 5.18          | 26234 |
| A8        | Langevatnet     | Hordaland        | 0.05                    | 16                   | 60.77        | 4.71          | 26190 |
| A9        | Storavatnet     | Hordaland        | 0.14                    | 24                   | 60.18        | 5.05          | 26964 |
| A10       | Litlevatnet     | Møre og Romsdal  | 0.02                    | 123                  | 62.40        | 5.61          | 30910 |
| A11       | Svartdalsvatnet | Oppland          | 0.59                    | 1018                 | 62.28        | 8.84          | 34660 |
| A12       | Breidsjøen      | Oslo             | 0.21                    | 248                  | 60.00        | 11.03         | 2514  |
| A13       | Østensjøvatnet  | Oslo             | 0.33                    | 107                  | 59.89        | 10.83         | 2513  |
| A14       | Tunevatnet      | Østfold          | 2.36                    | 40                   | 59.31        | 11.10         | 3451  |
| A15       | Vansjø          | Østfold          | 35.62                   | 25                   | 59.38        | 10.86         | 291   |
| A16       | Frøylandsvatnet | Rogaland         | 4.69                    | 24                   | 58.74        | 5.67          | 1552  |
| A17       | Måkevann        | Rogaland         | 0.28                    | 272                  | 58.32        | 6.38          | 21729 |
| A18       | Røyrvatnet      | Rogaland         | 0.43                    | 231                  | 59.54        | 6.03          | 22548 |
| A19       | Nystølsvatnet   | Sogn og Fjordane | 1.27                    | 715                  | 61.34        | 6.46          | 1651  |
| A20       | Skjervatjern    | Sogn og Fjordane | 0.02                    | 136                  | 61.43        | 6.04          | 28412 |
| A21       | Akersvatnet     | Vestfold         | 2.39                    | 16                   | 59.24        | 10.33         | 314   |
| S1        | Fedje Seawater  | Rogaland         | ~                       | 0                    | 60.78        | 4.70          | ~     |



**Figure 1.** Map showing locations of study lakes. Sites in this map (and in all others that follow) are labeled with the codes defined in Table 1.

The set of lakes that we selected are diverse; they differ in their water chemistry, their exposure to various human activities, as well as several other factors (see Table 2 for a summary of the relative influence of several factors on the selected study lakes). In particular, in our lake selection we have aimed to achieve the following gradients:

- A broad geographic distribution in southern Norway
- A range in lake elevation, lake area, lake depth and catchment area
- Differences in the prevalence of agriculture (both grain and animal), urbanization, and forested areas in lake catchments
- Differences in lake trophic status (including several eutrophic lakes)
- Differences in marine influence (i.e. proximity to the sea)
- Differences in humic content (lake colour) and pH
- Differences in macrophyte abundance
- Differences in the influence of seabirds

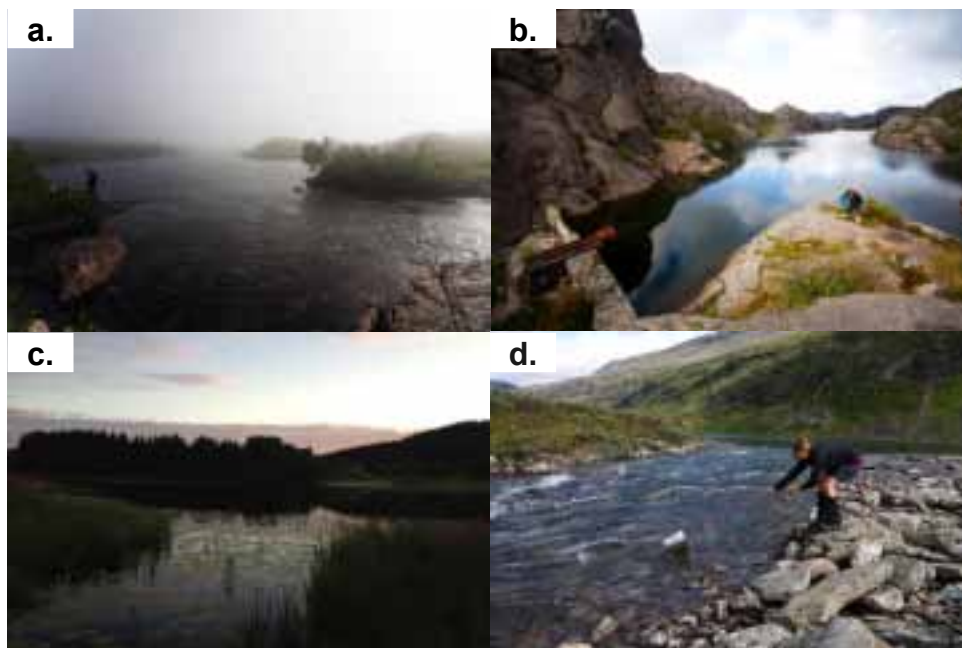
**Table 2.** Summary of factors influencing the study lakes (\*impacted and \*\*heavily impacted unless otherwise noted; agric: agriculture; urban: urbanization; eutro: eutrophication (\*\*TP (total phosphorus)>25 µg/L, \*10<TP<25 µg/L); macro: macrophytes; birds: bird influence; marine: marine influence (\*\*high CI and near sea); TOC: humic content (\*\*TOC>10 mg/L, 5<TOC<10 mg/L); acid: lake acidity (\*pH<5, \*5<pH<6); forest: forested catchment).

| Site | Lake                         | Agri            | Urban | Eutro          | Macro | Birds | Marine | TOC | Acid | Forest |
|------|------------------------------|-----------------|-------|----------------|-------|-------|--------|-----|------|--------|
| A1   | Spiradammen                  | * <sup>a</sup>  | *     | *              | **    |       |        | *   |      |        |
| A2   | Lille Hovvatnet              |                 |       |                |       |       |        |     | *    | *      |
| A3   | Langtjern                    |                 |       |                |       |       |        | **  | *    | *      |
| A4   | Steinsfjorden                | * <sup>a</sup>  |       | *              | *     |       |        |     |      |        |
| A5   | Atnsjøen                     |                 |       |                |       |       |        |     |      |        |
| A6   | Mjøsa                        | * <sup>a</sup>  | *     |                |       |       |        |     |      |        |
| A7   | Fonnestvatnet                | ** <sup>b</sup> |       | **             |       |       |        | **  |      |        |
| A8   | Langevatnet                  |                 |       | * <sup>e</sup> |       | *     | **     | *   | *    |        |
| A9   | Storavatnet                  |                 |       |                |       |       | **     |     | *    |        |
| A10  | Litlevatnet                  |                 |       | * <sup>e</sup> |       | **    | **     | *   |      |        |
| A11  | Svartdalsvatnet <sup>c</sup> |                 |       |                |       |       |        |     |      |        |
| A12  | Breidsjøen                   |                 |       |                |       |       |        |     |      | *      |
| A13  | Østensjøvatnet               |                 | **    | **             | *     | *     | *      | *   |      |        |
| A14  | Tunevatnet                   | ** <sup>a</sup> | *     | **             |       |       |        | *   |      |        |
| A15  | Vansjø                       | * <sup>a</sup>  |       | **             |       |       |        | *   |      |        |
| A16  | Frøylandsvatnet              | ** <sup>b</sup> |       | **             |       |       |        |     |      |        |
| A17  | Måkevann <sup>d</sup>        |                 |       |                |       |       |        |     | *    |        |
| A18  | Røyrvatnet                   |                 |       |                |       |       |        |     | *    | *      |
| A19  | Nystølsvatnet <sup>c</sup>   |                 |       |                |       |       |        |     | *    |        |
| A20  | Skjervatjern                 |                 |       |                |       |       |        | *   | **   | *      |
| A21  | Akersvatnet                  | ** <sup>b</sup> |       | **             |       |       |        | *   |      |        |
| S1   | Fedje Seawater               |                 |       |                |       |       | **     |     |      |        |

<sup>a</sup> primarily grain agriculture; <sup>b</sup> primarily animal agriculture; <sup>c</sup> alpine lake; <sup>d</sup> relatively high concentration of nitrates for a low nutrient lake; <sup>e</sup> despite high TP concentrations, phytoplankton biomass is low in these lakes.

## 2.2 Sample collection

Samples were collected between 26 July 2012 and 24 August 2012 using the same methodology as in NIVA's 2011 baseline survey at Mongstad (Grung et al. 2012). Water samples from all lakes were collected directly from the outflow (see Figure 2 for examples of outflow sampling sites). During autumn overturn, when the lake is fully mixed, sampling from a lake outflow should theoretically yield a sample that is fairly representative of the lake as a whole. However, during summer stratification, outflow water may be more representative of epilimnetic (upper water column) conditions.



**Figure 2.** Examples of lake outflow sampling sites (a. Nystølsvatnet (A19), b. Måkevann (A17), c. Fonnebostvatnet (A7), and d. Svartdalsvatnet (A11)).

Water was collected using an acetone-cleaned stainless steel bucket, and transferred to sample containers (dark 1 L polyethylene bottles for chlorophyll *a* analysis, regular 1 L polyethylene bottles for analysis of major chemical components, and 2.5 L dark glass bottles for analysis of amines). Water samples were kept in a dark and cold (~4–10 °C) environment during transport, and water samples for analysis of amines were delivered to NILU within 48 hours of collection. Meanwhile, within 12 hours of sampling, water for chlorophyll *a* analysis was filtered onto GF/C filters (nominal pore size of 0.7 µm) which were frozen until analysis.

## 2.3 Chemical analysis

### 2.3.1 General water chemistry

Analysis of major chemical components (TOC, pH, TP, TN, SO<sub>4</sub>, NO<sub>3</sub>, Cl and Na) and chlorophyll *a* (as a measure of phytoplankton biomass) was carried out at NIVA (see Table 3 for a summary of analytical methods and limits of detection). These parameters were included in order to characterize both the general water chemistry (including nutrient concentrations, humic matter/water colour, acidity and major ion concentrations) as well as trophic status of the study lakes.

**Table 3.** Summary of analytical methods and limits of detection (LOD) for surface water chemical analyses at NIVA.

| Code            | Parameter            | Analytical method                                             | LOD  | Unit                 |
|-----------------|----------------------|---------------------------------------------------------------|------|----------------------|
| pH              | pH                   | Potentiometry                                                 | ~    | ~                    |
| TOC             | Total organic carbon | UV/persulphate oxidation to CO <sub>2</sub><br>+ IR-detection | 0.10 | mg C L <sup>-1</sup> |
| TN              | Total nitrogen       | Automated photometry                                          | 10   | µg N L <sup>-1</sup> |
| TP              | Total phosphorus     | Automated photometry                                          | 1    | µg P L <sup>-1</sup> |
| NO <sub>3</sub> | Nitrate              | Ion chromatography                                            | 1    | µg N L <sup>-1</sup> |
| Na              | Sodium               | Ion chromatography                                            | 0.02 | mg L <sup>-1</sup>   |
| Cl              | Chloride             | Ion chromatography                                            | 0.03 | mg L <sup>-1</sup>   |
| SO <sub>4</sub> | Sulphate             | Ion chromatography                                            | 0.04 | mg L <sup>-1</sup>   |
| Chl <i>a</i>    | Chlorophyll <i>a</i> | Acetone extraction +<br>spectrophotometry                     | 0.31 | µg L <sup>-1</sup>   |



### 2.3.2 Amines

Analysis of seven amines of interest (methylamine, ethylamine, dimethylamine, diethylamine, monoethanolamine, 2-amino-2-methyl-propanol, and piperazine) was carried out at NILU. These seven amines are the same compounds that were measured in the 2011 baseline survey (Grung et al. 2012). These analyses were performed using NILU's in-house validated method, which is based on using derivatization to improve the analyte behavior towards reversed phase chromatography (see Table 4 for a summary of limits of detection for the seven amines analyzed).

Aliquots of the water samples were prepared by adding a buffer solution and the derivatizing agent. After a defined reaction time, sample analysis was carried out on a Waters UPLC liquid chromatography system equipped with an auto-sampler and a Waters LCT Premier XE mass spectrometer. Three parallel replicate subsamples were run for each lake sample, and ten replicates of tap and ultrapure (Milli Q) water were run as reference samples.

**Table 4.** Summary of analytical limits of detection (LOD) for amines measured at NILU. See section 4.3.3 for a description of the method used to determine LOD values for amine analyses.

| Code | Compound                  | LOD<br>(ng L <sup>-1</sup> ) |
|------|---------------------------|------------------------------|
| MA   | methylamine               | 10                           |
| EA   | ethylamine                | 40                           |
| MEA  | monoethanolamine          | 10                           |
| DMA  | dimethylamine             | 10                           |
| DEA  | diethylamine              | 50                           |
| AMP  | 2-amino-2-methyl-propanol | 100                          |
| PIP  | piperazine                | 10                           |

### 2.3.3 Calculations and statistical analyses

Limits of detection (LOD) for amines were determined based on signal to noise ratios (S/N) in the analytical chromatograms (these represent "method LOD" values). The LOD for each analyte was defined as  $S/N = 3$ .

We used Pearson's correlations ( $r$ ) to identify statistically significant relationships between measured parameters (including both water chemistry and amine concentrations). Prior to inclusion in correlation analysis, water chemistry and amine concentration data were log-transformed to achieve a normal distribution (based on the Shapiro-Wilks test,  $\alpha = 0.05$ ). Values for pH and TOC were not transformed, since these data were already normally distributed.

### 3. Results and Discussion

#### 3.1 General site chemistry

Based on the results of analysis of general water chemistry (Table 5), we found that the sites chosen covered a wide range in major component water chemistry and spanned several gradients in the influence of both natural and anthropogenic drivers including eutrophication, prevalence of wetlands in the catchment, and acidification.

**Table 5.** Results from analysis of major chemical components and chlorophyll *a* (as a measure of phytoplankton biomass) in water from the study sites.

| Site | pH   | TP<br>(ug/L) | TN<br>(ug/L) | NO <sub>3</sub><br>(ug/L) | TOC<br>(mg/L) | Na<br>(mg/L) | Cl<br>(mg/L) | SO <sub>4</sub><br>(mg/L) | Chl <i>a</i><br>(ug/L) |
|------|------|--------------|--------------|---------------------------|---------------|--------------|--------------|---------------------------|------------------------|
| A1   | 7.97 | 13           | 450          | 1                         | 5.9           | 7.6          | 8.4          | 17.8                      | 1.8                    |
| A2   | 5.41 | 5            | 320          | 25                        | 4.3           | 1.19         | 1.72         | 1.02                      | 0.78                   |
| A3   | 5.24 | 5            | 270          | 1                         | 11.7          | 0.51         | 0.38         | 0.55                      | 1.40                   |
| A4   | 7.61 | 11           | 305          | 12                        | 3.5           | 4.01         | 5.17         | 6.16                      | 4.9                    |
| A5   | 6.61 | 4            | 103          | 11                        | 1.3           | 0.36         | 0.25         | 0.71                      | 2.5                    |
| A6   | 7.36 | 4            | 440          | 270                       | 2.1           | 1.13         | 1.61         | 3.92                      | 3.1                    |
| A7   | 6.32 | 33           | 605          | <1                        | 11.2          | 6.1          | 8.97         | 4                         | 2.6                    |
| A8   | 5.06 | 16           | 255          | 1                         | 5.2           | 19.3         | 35.1         | 4.99                      | 1.5                    |
| A9   | 5.98 | 5            | 185          | 1                         | 3             | 12.1         | 21.9         | 3.32                      | 1.2                    |
| A10  | 6.93 | 18           | 370          | 1                         | 7.8           | 21.4         | 37.9         | 3.61                      | 1.8                    |
| A11  | 6.43 | 1            | 70           | 21                        | 0.33          | 0.33         | 0.36         | 0.51                      | 0.61                   |
| A12  | 7.37 | 3            | 215          | 23                        | 3.1           | 1.76         | 1.83         | 2.73                      | 1.30                   |
| A13  | 7.48 | 131          | 1140         | 6                         | 7.5           | 23.7         | 38.8         | 9.78                      | 80                     |
| A14  | 6.64 | 31           | 490          | <1                        | 5.3           | 10.1         | 15.5         | 5.71                      | 12                     |
| A15  | 6.88 | 29           | 760          | 260                       | 8.3           | 8.14         | 12.8         | 5.74                      | 10                     |
| A16  | 7.55 | 25           | 950          | 380                       | 4.4           | 10.3         | 18.2         | 6.52                      | 18                     |
| A17  | 5.92 | 5            | 380          | 185                       | 1.8           | 6.41         | 11.1         | 5.04                      | 1.3                    |
| A18  | 5.92 | 2            | 165          | 47                        | 2.1           | 1.62         | 2.33         | 0.94                      | 0.7                    |
| A19  | 5.90 | 1            | 77           | 34                        | 0.34          | 1            | 1.67         | 0.54                      | <0.31                  |
| A20  | 4.74 | 5            | 225          | 1                         | 7.3           | 3.6          | 7.14         | 0.88                      | 2.2                    |
| A21  | 7.59 | 56           | 1410         | 625                       | 6.7           | 13.1         | 20.5         | 10.7                      | 26                     |
| S1   | 8.09 | 10           | 195          | 2                         | 2             | 2200         | 15900        | 2200                      | 1.1                    |

Some of the natural and anthropogenic (e.g. pollution) factors likely to be important determinants of water chemistry in the study lakes are summarized in Table 6 and are described in the text that follows.

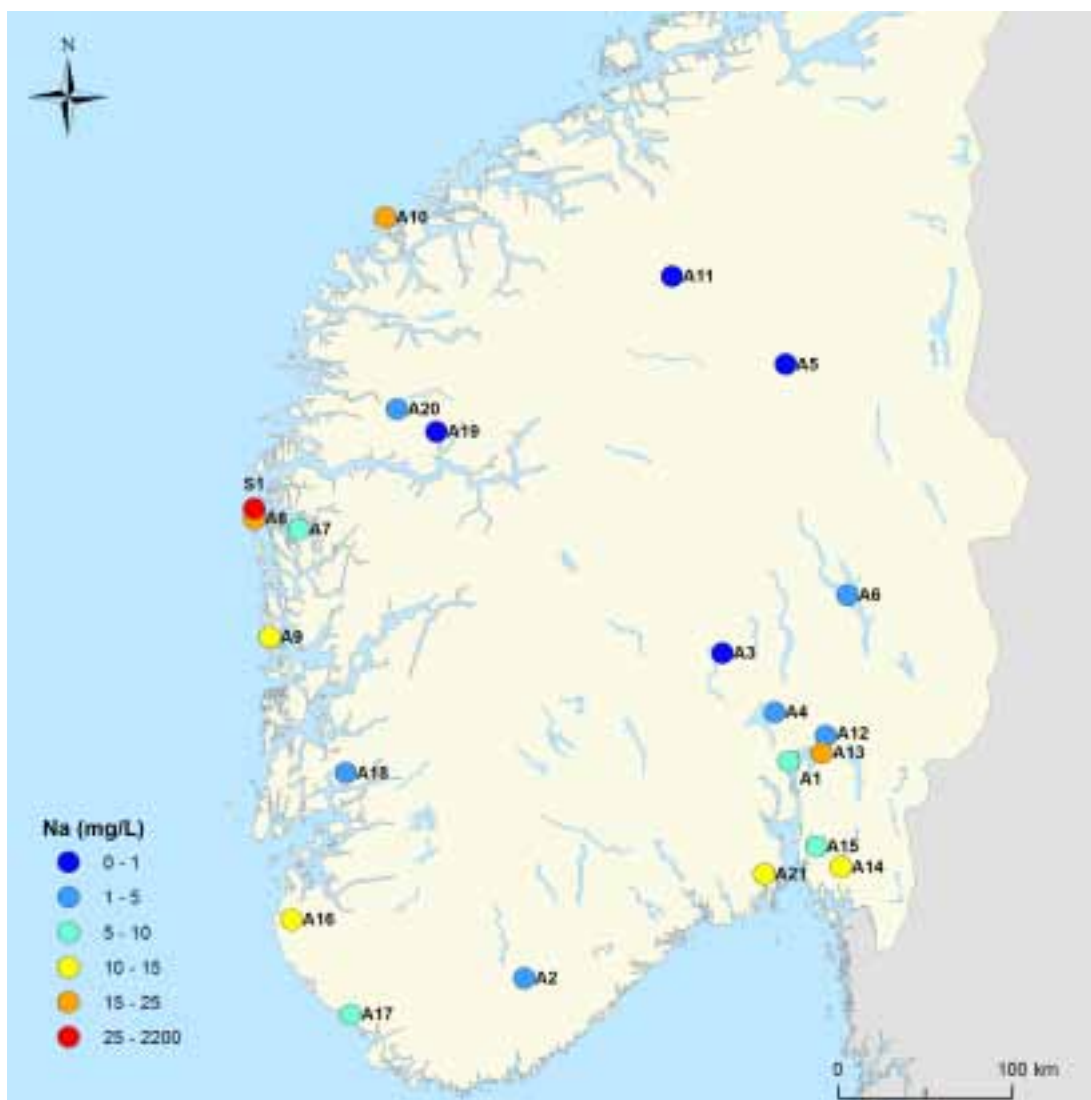
**Table 6.** Select factors affecting the chemical composition of natural waters, with examples of chemical parameters affected, and sites influenced by these factors. Codes used are defined in Tables 1 and 3.

| Factor                                                | Type      | Chemical signals               | Site examples                                             |
|-------------------------------------------------------|-----------|--------------------------------|-----------------------------------------------------------|
| Seasalts (atmospheric deposition)                     | Natural   | High Cl, Na, SO <sub>4</sub>   | Ma (A17), Sto (A9), Lit (A10)                             |
| De-icing road salts (from terrestrial catchment)      | Pollution | High Cl, Na                    | Os (A13)                                                  |
| Humic runoff (from terrestrial catchment)             | Natural   | High TOC (low pH)              | Ln (A3), Sk (A20), Fo (A7)                                |
| Acidification (deposition of S and N)                 | Pollution | Low pH, high SO <sub>4</sub>   | Lil (A2), Ln (A3)                                         |
| Eutrophication (nutrients from terrestrial catchment) | Pollution | High TP, TN, TOC, Chl <i>a</i> | Os (A13), Tu (A14), Va (A15), Fr (A16), Ak (A21), Fo (A7) |

### 3.1.1 Na, Cl and SO<sub>4</sub>

Lakes near the coast usually have high concentrations of chloride (Cl) and sodium (Na), as well as elevated concentrations of both magnesium (Mg) and sulphate (SO<sub>4</sub>). This is due to natural seaspray that is entrained into the atmosphere, transported to the land and deposited in wet and dry deposition. In Norway the seasalt influence decreases with distance from the coast and is minor after 10-20 km inland. In the current study, several of the coastal study lakes had particularly high Na, Cl and SO<sub>4</sub> concentrations (Table 5, Figure 3).

Østensjøvatnet (A13) also had very high Na and Cl concentrations, despite having less of a marine influence than many of the coastal lakes. This is likely due to localized application of road salts, given that Østensjøvatnet is an urban lake (within Oslo) that is bordered by a large road.



**Figure 3.** Na concentrations in the study lakes.

### 3.1.2 Organic matter

Organic matter in lakes can come from several natural or anthropogenic sources. Particularly important sources of organic matter to lakes includes humic-rich runoff from natural forests or peatlands (allochthonous carbon), or organic matter produced within the lake by algae (autochthonous carbon). High levels of dissolved organic matter are characterized by high concentrations of TOC as well as other nutrients such as TN. The dissolved organic matter in humic-rich runoff contains organic acids, which can act to lower the pH in highly coloured waters.

In the current study, TOC concentrations ranged from 0.33 to 11.7 mg/L (Table 5, Figure 4), with the highest concentrations occurring in lakes that have either substantial wetland areas in their catchment (e.g. Langtjern (A3) or Skjervatjern (A20)) or high levels of phytoplankton productivity (e.g. Østensjøvatnet (A13) and Vansjø (A15)).

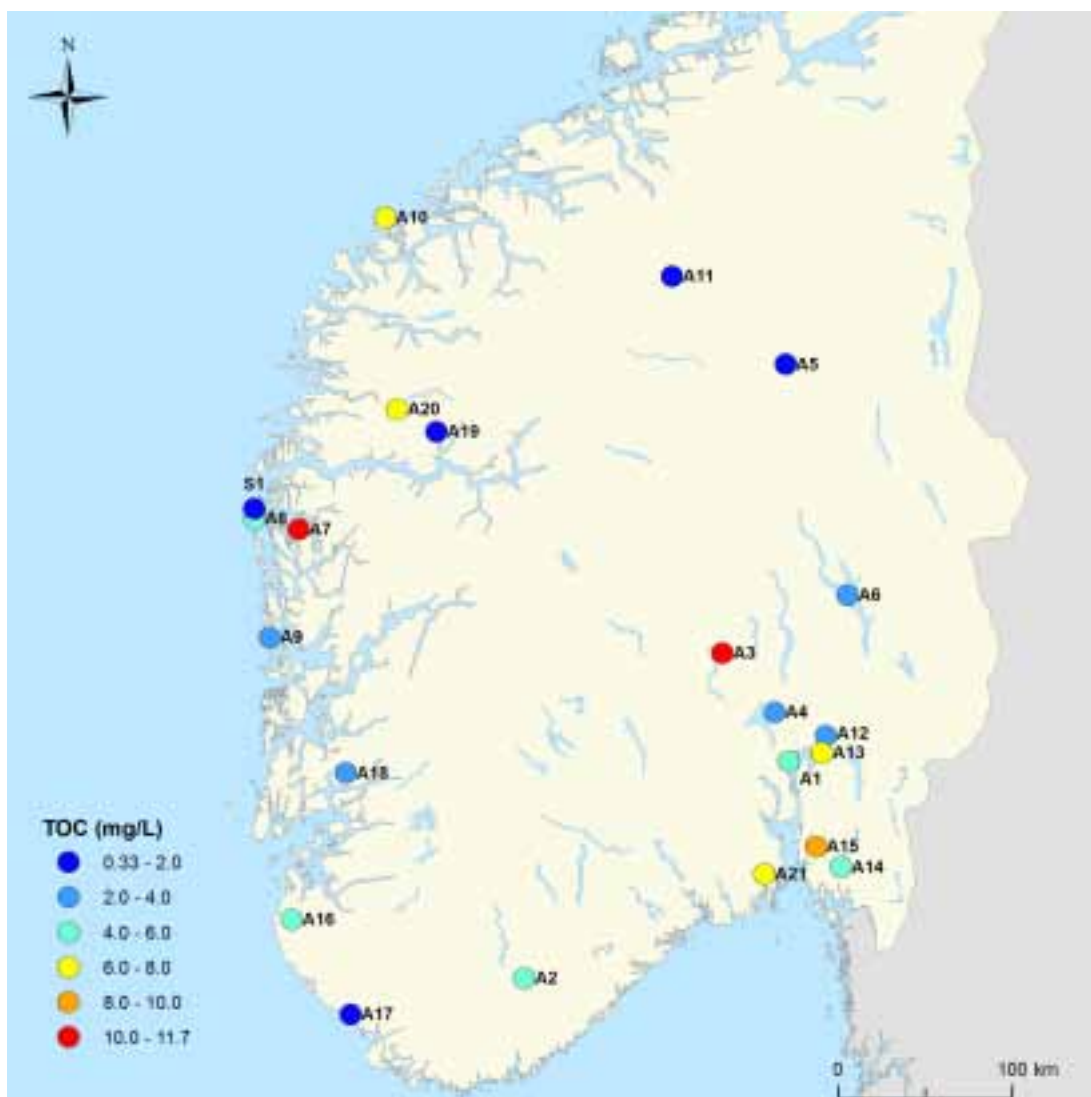


Figure 4. TOC concentrations in the study lakes.

### 3.1.3 Acidification

Deposition of sulphur and nitrogen components from the atmosphere (acid deposition) leads to acidification of soils, runoff and surface waters. Acidified waters have low pH and elevated concentrations of sulphate, and sometimes also nitrate, as well as high levels of inorganic aluminium species that are toxic to fish and other organisms.

The study lakes ranged in pH from 4.74 to 7.97 (Table 5, Figure 5; although the seawater reference site had a pH of 8.09). The lowest pH values were typically observed for poorly buffered humic lakes with a history of anthropogenic acidification (such as Lille Hovvatnet (A2) and Langtjern (A3)).

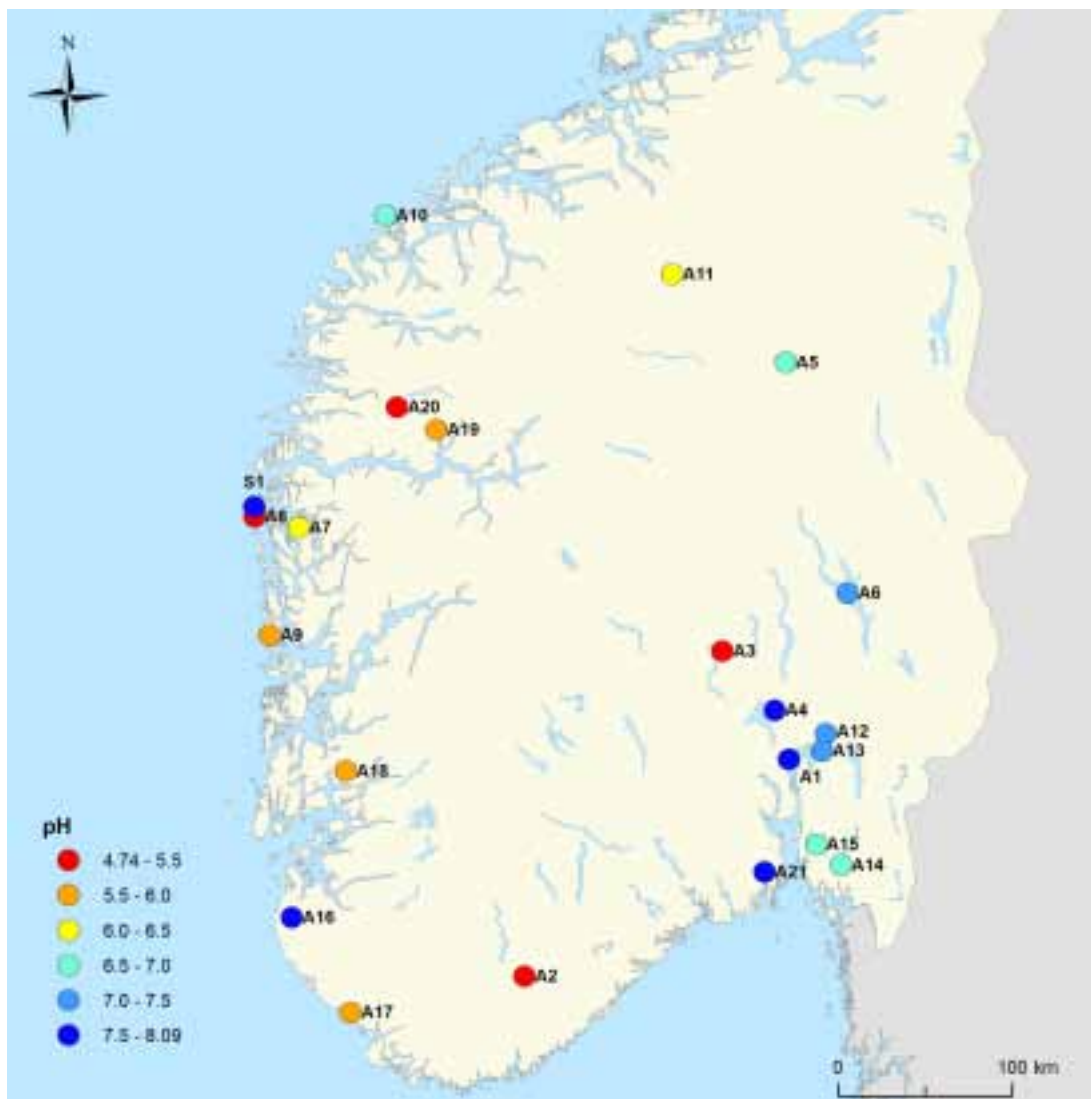


Figure 5. pH of the study lakes.

### 3.1.4 Eutrophication

Pollution by nutrients from agriculture and human wastewaters leads to elevated concentrations of phosphorus and nitrogen. Primary production in most Norwegian lakes is limited by phosphorus, and lakes with high concentrations of phosphorus typically have high biomasses of phytoplankton (reflected in concentrations of the pigment chlorophyll *a*) and /or higher aquatic plants (macrophytes). The high biomasses of primary producers can also lead to high TOC in these lakes.

Lakes are often categorized based on their trophic status (or productivity) based on their nutrient or chlorophyll *a* concentrations. “Oligotrophic” lakes are typically clear, unproductive lakes with low nutrient concentrations and phytoplankton biomass (often defined as a lake where TP < 10 µg/L and/or Chl *a* < 2.5 µg/L), “mesotrophic” lakes are intermediately productive (10 < TP < 35 µg/L and/or 2.5 < Chl *a* < 8 µg/L), “eutrophic” lakes are often defined as have TP concentrations between 35–100 µg/L and/or chlorophyll *a* concentrations between 8–25 µg/L. Lakes with TP and/or chlorophyll *a* concentrations in excess of these ranges are defined as “hypereutrophic”.

Of the sites included in the current study, based on TP and chlorophyll *a* concentrations, more than half of the study lakes can be classified as oligotrophic (Table 5, Figures 6, 7), while only a small subset of the lakes were eutrophic or hypereutrophic (e.g. Østensjøvatnet (A13) and Akersvatnet (A21)). The remaining sites can be classified as mesotrophic.

In particular, lakes heavily influenced by urbanization and/or agriculture tended to have the highest nutrient (TN, TP) and chlorophyll *a* concentrations (see Table 2 for a summary of agricultural and urban influences on the study lakes and their catchments). Meanwhile, the lowest concentrations were observed in dilute and remote lakes without significant inputs of organic matter (or nutrients) from their catchments, such as the alpine lakes Svartdalsvatnet (A11) and Nystølsvatnet (A19).

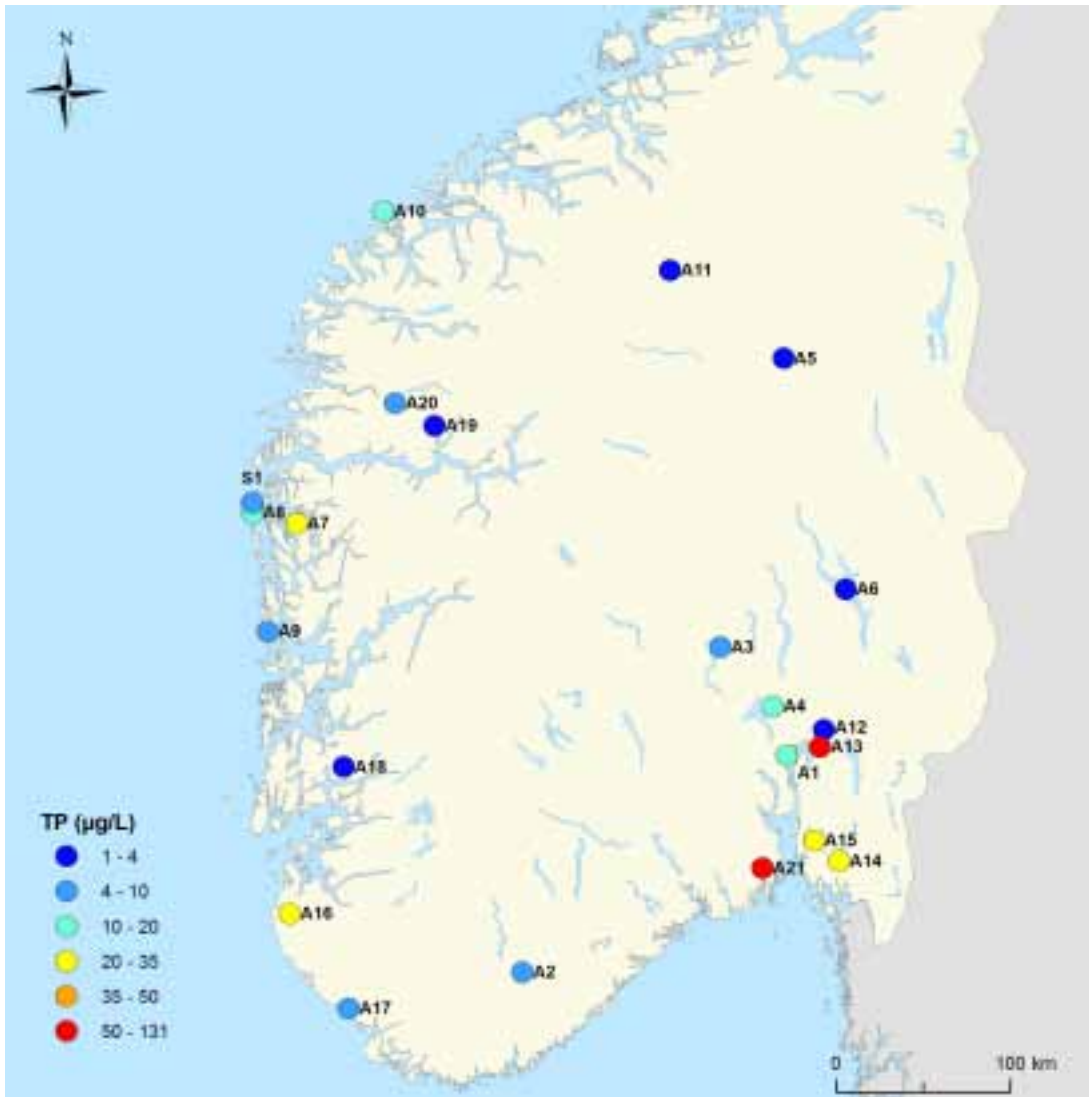


Figure 6. TP concentrations in the study lakes.



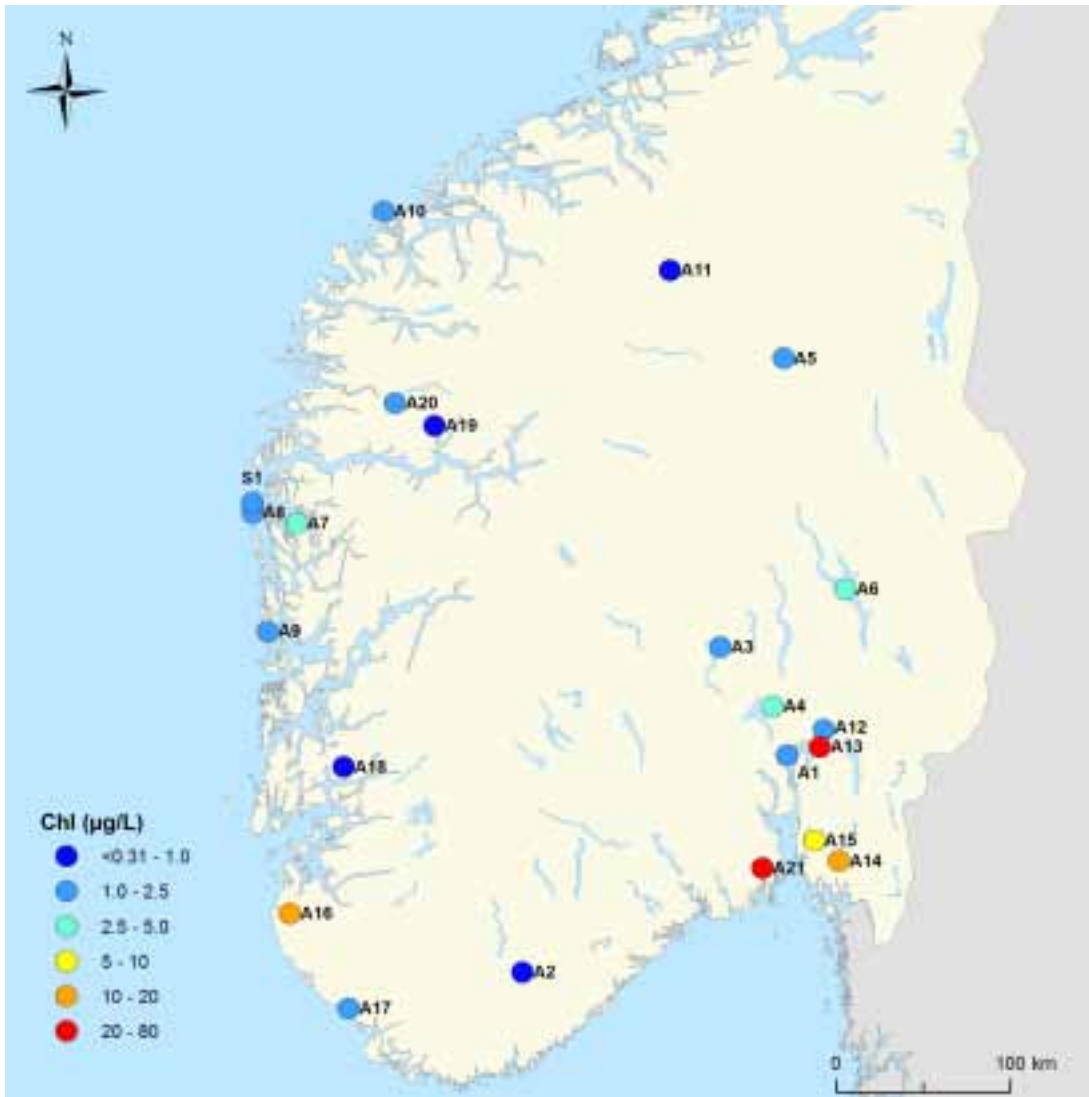


Figure 7. Chlorophyll *a* concentrations (as an indicator of phytoplankton biomass) in the study lakes.

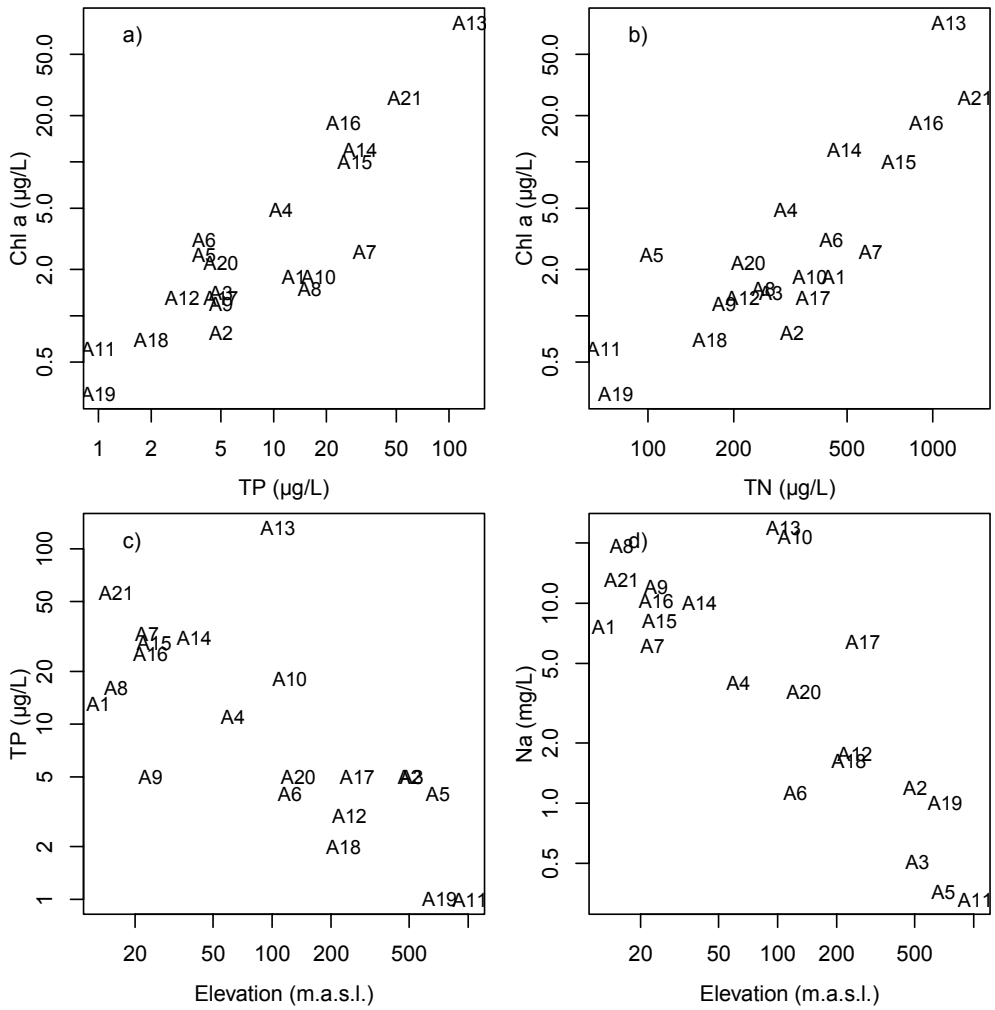
### 3.2 Relationships between water chemistry parameters

Among the water chemistry parameters measured, there were significant positive correlations (Table 7) between chlorophyll *a* concentrations and total phosphorus and nitrogen concentrations (Figure 8a, b), with higher nutrient concentrations supporting higher biomasses of phytoplankton. Concentrations of TP, TN and chlorophyll *a* were also positively related to concentrations of marine derived ions and negatively related to elevation (Figure 8c). This is likely due to the fact that lowland and coastal lakes in southern Norway are often situated in an agricultural landscape with higher population densities, thus are more prone to increases in nutrient loading and trophic status.

There were also significant positive correlations (Table 7) between Na, Cl and SO<sub>4</sub> concentrations, driven by the co-occurrence of these ions in water influenced by deposition of marine derived ions (from seaspray). We also found strong negative correlations between these three ions and elevation (Figure 8d), which can also be attributed to differences in marine influence between low-lying coastal areas and higher elevation lakes (which were typically further inland).

**Table 7.** Pearson's correlation coefficients (*r*) for correlations between water chemistry parameters for freshwater samples. Correlations shown are significant at the P<0.05 level. Values marked with an asterisk are significant at the P<0.01 level.

|                 | pH    | TP     | TN     | NO <sub>3</sub> | TOC | Na     | Cl     | SO <sub>4</sub> | Chl <i>a</i> |
|-----------------|-------|--------|--------|-----------------|-----|--------|--------|-----------------|--------------|
| pH              | 1     |        |        |                 |     |        |        |                 |              |
| TP              |       | 1      |        |                 |     |        |        |                 |              |
| TN              | 0.47  | *0.89  | 1      |                 |     |        |        |                 |              |
| NO <sub>3</sub> |       |        |        | 1               |     |        |        |                 |              |
| TOC             |       | *0.64  | *0.58  | -0.45           | 1   |        |        |                 |              |
| Na              |       | *0.79  | *0.69  |                 |     | 1      |        |                 |              |
| Cl              |       | *0.74  | *0.66  |                 |     | *0.99  | 1      |                 |              |
| SO <sub>4</sub> | *0.65 | *0.78  | *0.79  |                 |     | *0.81  | *0.77  | 1               |              |
| Chl <i>a</i>    | *0.55 | *0.87  | *0.72  |                 |     | *0.57  | 0.53   | *0.66           | 1            |
| Elevation       |       | *-0.71 | *-0.67 |                 |     | *-0.80 | *-0.77 | *-0.82          | -0.52        |



**Figure 8.** Select correlations between water chemistry parameters: a) chlorophyll *a* vs. TP, b) chlorophyll *a* vs. TN, c) TP vs. elevation, and d) Na vs. elevation. See Table 7 for Pearson’s correlation coefficients.

### 3.3 Amines in Norwegian lakes

#### 3.3.1 Amine Concentrations

There are very few reported concentrations of amines in surface waters in the scientific literature. As such, the current study represents an important source of information about the prevalence of these compounds in freshwater systems. In particular, the inclusion of several remote lakes with low levels of human impact should yield an estimate of the range of background amine concentrations that exist in Norwegian freshwaters. Furthermore, the pairing of analysis for select amines with characterization of general water chemistry and primary productivity allows us to test for relationships between lake characteristics, human and natural influences and amine concentrations.

We measured seven different amines in water from all study sites: methylamine (MA), ethylamine (EA), monoethanolamine (MEA), dimethylamine (DMA), diethylamine (DEA), 2-amino-2-methylpropanol (AMP) and piperazine (PIP). Results from analysis of tap and MilliQ water (Table 8) revealed high concentrations of several amines, even in these “reference samples”.

**Table 8.** Concentrations (mean  $\pm$  s.d. in ng/L) of amines in tap and MilliQ and tap water references. Results are for 10 replicates, run in parallel.

|              | MA           | EA  | MEA            | DMA            | DEA         | AMP  | PIP          |
|--------------|--------------|-----|----------------|----------------|-------------|------|--------------|
| MilliQ Water | 911 $\pm$ 46 | <40 | 993 $\pm$ 109  | 8718 $\pm$ 959 | 98 $\pm$ 22 | <100 | 589 $\pm$ 71 |
| Tap Water    | 725 $\pm$ 36 | <40 | 1048 $\pm$ 105 | 3154 $\pm$ 284 | <50         | <100 | 712 $\pm$ 85 |

There are two possible explanations for these elevated values: 1) this may be a methodological artefact (e.g. contamination during the analytical procedure or interference by one of the reagents); or 2) these measured concentrations may be true concentrations, and suggest that these reference samples were not “amine free”, given the prevalence of amines in all environments (one possibility could be bacterial contamination of these water sources). If these elevated values represent a methodological artefact, then these values should be treated as true blanks and subtracted from the amine concentrations observed in the surface water samples, while if it assumed that these concentrations are true concentrations and that tap and MilliQ water were not amine free, then the raw surface water data should be used in further analysis. It is also important to note that these two possible explanations are not mutually exclusive.

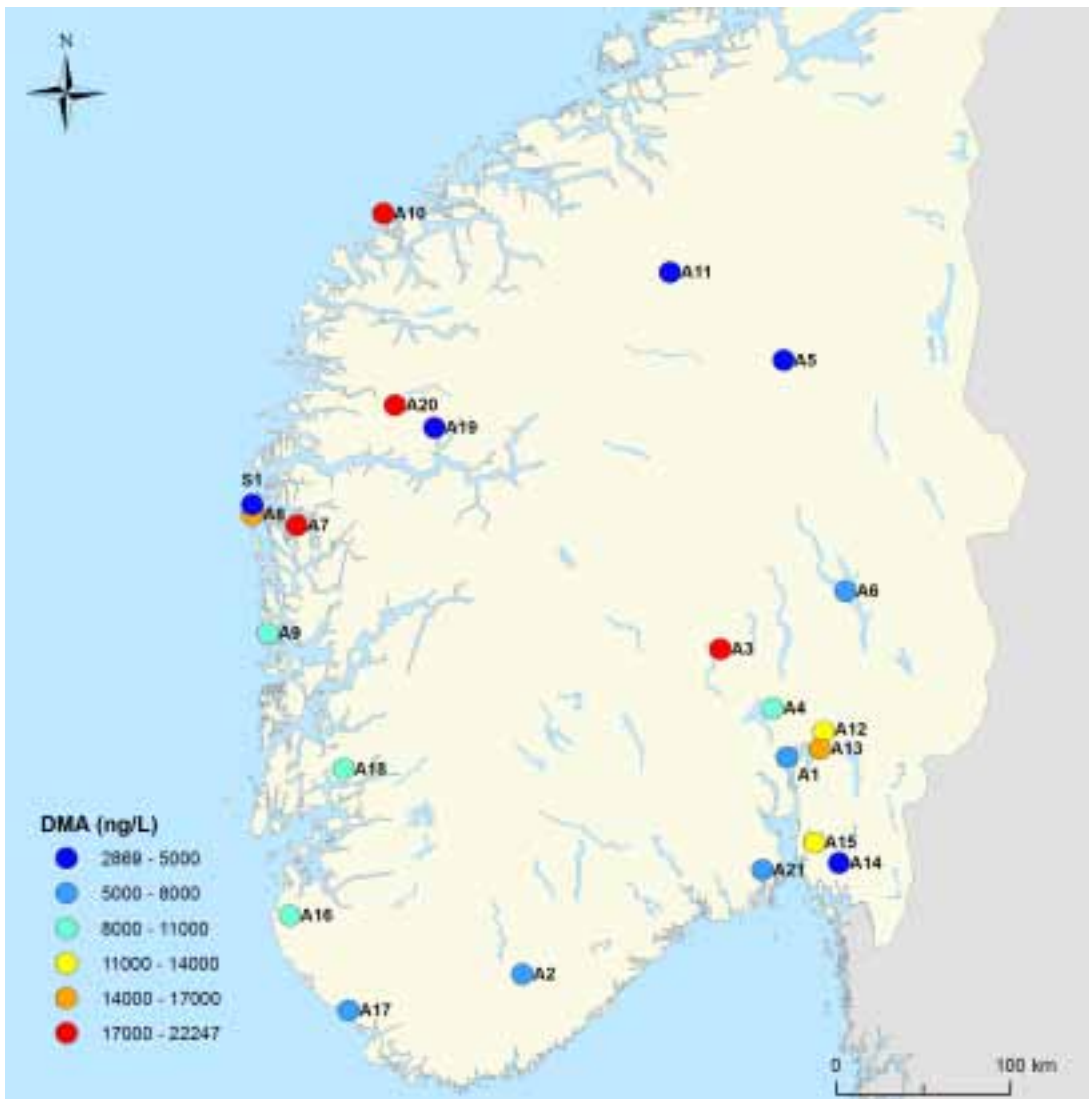
NILU has suggested that we treat the MilliQ and tap water results as references, rather than blanks, and as such, these values have not been subtracted from the results reported in Table 9, Figures 9–13 or in the statistical analyses that follow. However, given the uncertainty surrounding the interpretation of these elevated reference values, in section 5.3.3 we will assess (and discuss) how the results and relationships found differ if we are to assume that the values in Table 8 represent true blanks and should therefore be subtracted from amine concentrations in surface waters (the values in Table 9).

The most prevalent amine at all study sites was DMA, a secondary aliphatic amine (range: 2 869–22 247 ng/L, Table 9, Figure 9). MA and MEA concentrations were also high, ranging from 327–4 946 ng/L and 686–4 435 ng/L respectively (Figures 10, 11). Intermediate concentrations were observed for PIP (454–842 ng/L, Figure 12) and DEA (<50–960 ng/L, Figure 13), while EA and AMP were not detected in water from any of the sites. Concentrations of the measured amines were highly variable

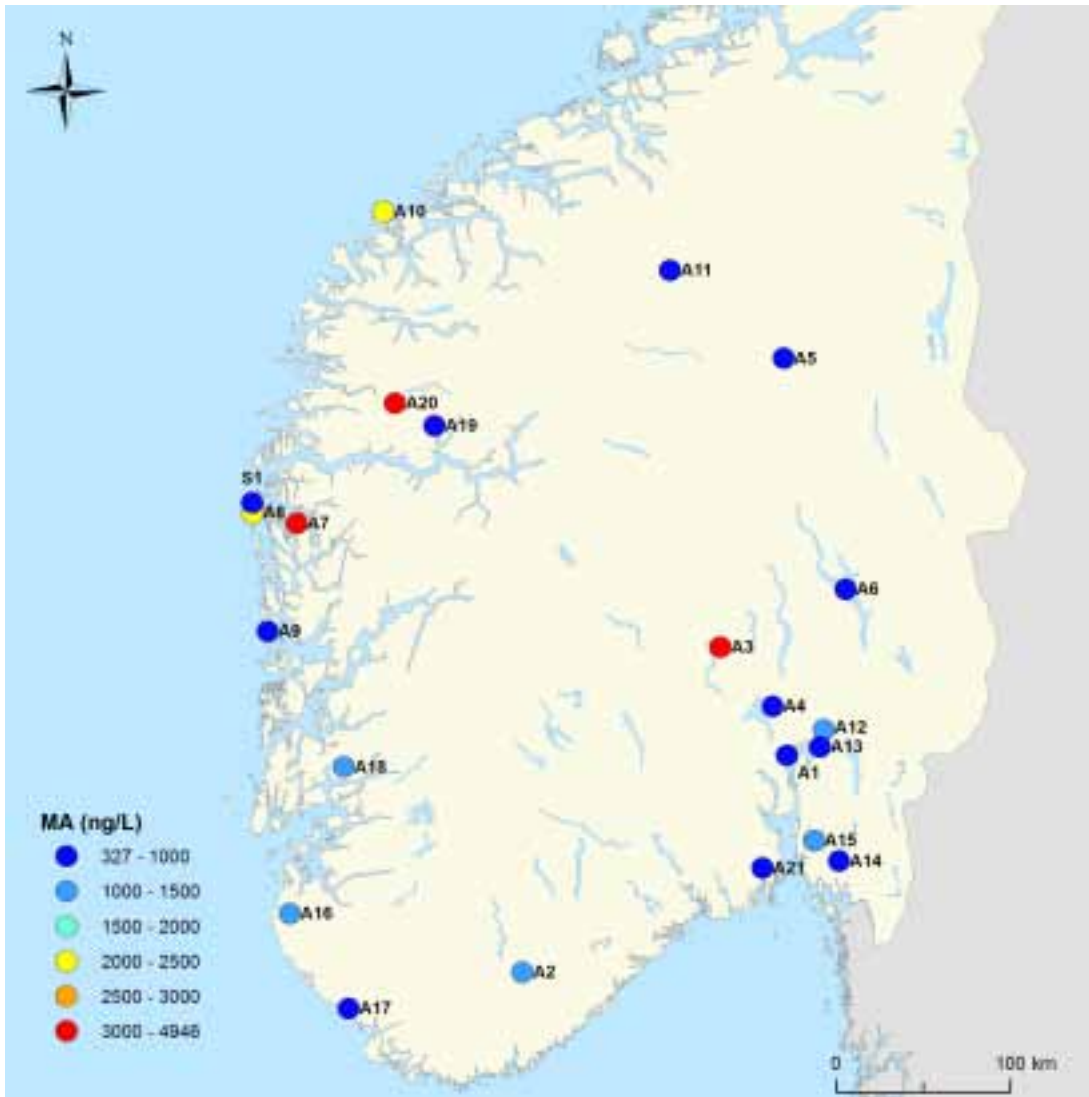
across all study sites, and were also somewhat variable between replicate runs of the same sample, possibly suggesting intra-sample heterogeneity of amine concentrations (which could reflect the presence of heterogeneously distributed particulate organic matter, such as phytoplankton).

**Table 9.** Concentrations (mean  $\pm$  s.d. in ng/L) of amines in water (MA: methylamine; EA: ethylamine; MEA: monoethanolamine; DMA: dimethylamine; DEA: diethylamine; AMP: 2-amino-2-methylpropanol; and PIP: piperazine). Results are for triplicate sample runs (with the exception of sites A2, A17, and A21, where duplicate results are reported).

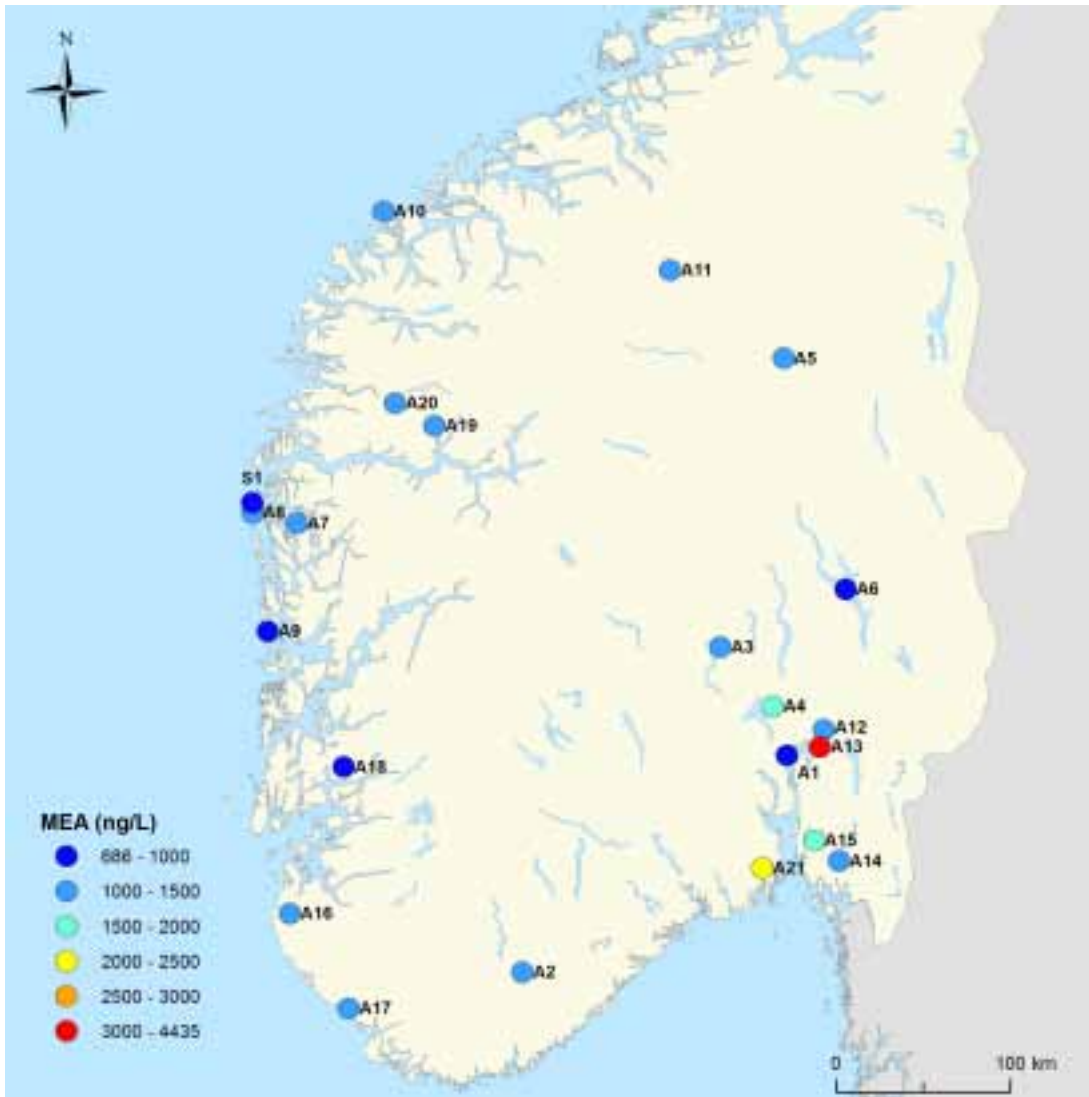
| Site | MA             | EA  | MEA            | DMA              | DEA          | AMP  | PIP           |
|------|----------------|-----|----------------|------------------|--------------|------|---------------|
| A1   | 630 $\pm$ 111  | <40 | 856 $\pm$ 96   | 7874 $\pm$ 774   | 128 $\pm$ 8  | <100 | 506 $\pm$ 228 |
| A2   | 1452 $\pm$ 140 | <40 | 1072 $\pm$ 3   | 6537 $\pm$ 300   | 960 $\pm$ 93 | <100 | 466 $\pm$ 10  |
| A3   | 4946 $\pm$ 371 | <40 | 1168 $\pm$ 192 | 22247 $\pm$ 522  | 83 $\pm$ 9   | <100 | 628 $\pm$ 138 |
| A4   | 867 $\pm$ 72   | <40 | 1640 $\pm$ 453 | 9403 $\pm$ 332   | 113 $\pm$ 28 | <100 | 523 $\pm$ 163 |
| A5   | 782 $\pm$ 167  | <40 | 1239 $\pm$ 617 | 4906 $\pm$ 628   | 90 $\pm$ 8   | <100 | 677 $\pm$ 264 |
| A6   | 748 $\pm$ 29   | <40 | 934 $\pm$ 75   | 5468 $\pm$ 586   | 79 $\pm$ 17  | <100 | 455 $\pm$ 132 |
| A7   | 3709 $\pm$ 289 | <40 | 1048 $\pm$ 131 | 18538 $\pm$ 666  | 56 $\pm$ 1   | <100 | 474 $\pm$ 264 |
| A8   | 2171 $\pm$ 64  | <40 | 1054 $\pm$ 140 | 14554 $\pm$ 490  | 204 $\pm$ 15 | <100 | 580 $\pm$ 207 |
| A9   | 885 $\pm$ 65   | <40 | 897 $\pm$ 140  | 8165 $\pm$ 825   | 86 $\pm$ 19  | <100 | 725 $\pm$ 147 |
| A10  | 2314 $\pm$ 135 | <40 | 1032 $\pm$ 160 | 17245 $\pm$ 380  | 68 $\pm$ 18  | <100 | 454 $\pm$ 265 |
| A11  | 572 $\pm$ 65   | <40 | 1022 $\pm$ 222 | 3351 $\pm$ 433   | 57 $\pm$ 19  | <100 | 642 $\pm$ 197 |
| A12  | 1273 $\pm$ 130 | <40 | 1181 $\pm$ 50  | 13646 $\pm$ 482  | 73 $\pm$ 10  | <100 | 601 $\pm$ 232 |
| A13  | 913 $\pm$ 25   | <40 | 4435 $\pm$ 303 | 14343 $\pm$ 1965 | 63 $\pm$ 3   | <100 | 513 $\pm$ 252 |
| A14  | 688 $\pm$ 61   | <40 | 1431 $\pm$ 83  | 4429 $\pm$ 386   | 73 $\pm$ 12  | <100 | 593 $\pm$ 181 |
| A15  | 1128 $\pm$ 82  | <40 | 1863 $\pm$ 51  | 12574 $\pm$ 886  | 76 $\pm$ 4   | <100 | 539 $\pm$ 104 |
| A16  | 1085 $\pm$ 150 | <40 | 1311 $\pm$ 177 | 9952 $\pm$ 2273  | 180 $\pm$ 25 | <100 | 532 $\pm$ 263 |
| A17  | 786 $\pm$ 111  | <40 | 1174 $\pm$ 198 | 5435 $\pm$ 600   | 109 $\pm$ 12 | <100 | 624 $\pm$ 168 |
| A18  | 1089 $\pm$ 100 | <40 | 896 $\pm$ 135  | 8319 $\pm$ 939   | 67 $\pm$ 7   | <100 | 556 $\pm$ 308 |
| A19  | 656 $\pm$ 95   | <40 | 1027 $\pm$ 372 | 3743 $\pm$ 703   | 67 $\pm$ 29  | <100 | 531 $\pm$ 237 |
| A20  | 3830 $\pm$ 262 | <40 | 1037 $\pm$ 96  | 19616 $\pm$ 702  | 114 $\pm$ 16 | <100 | 606 $\pm$ 303 |
| A21  | 659 $\pm$ 6    | <40 | 2075 $\pm$ 183 | 7865 $\pm$ 461   | 110 $\pm$ 8  | <100 | 462 $\pm$ 264 |
| S1   | 327 $\pm$ 31   | <40 | 686 $\pm$ 58   | 2869 $\pm$ 232   | <50          | <100 | 842 $\pm$ 210 |



**Figure 9.** Concentrations of DMA in the study lakes. MilliQ and tap water references had mean concentrations of 8 718 and 3 154 ng/L respectively.

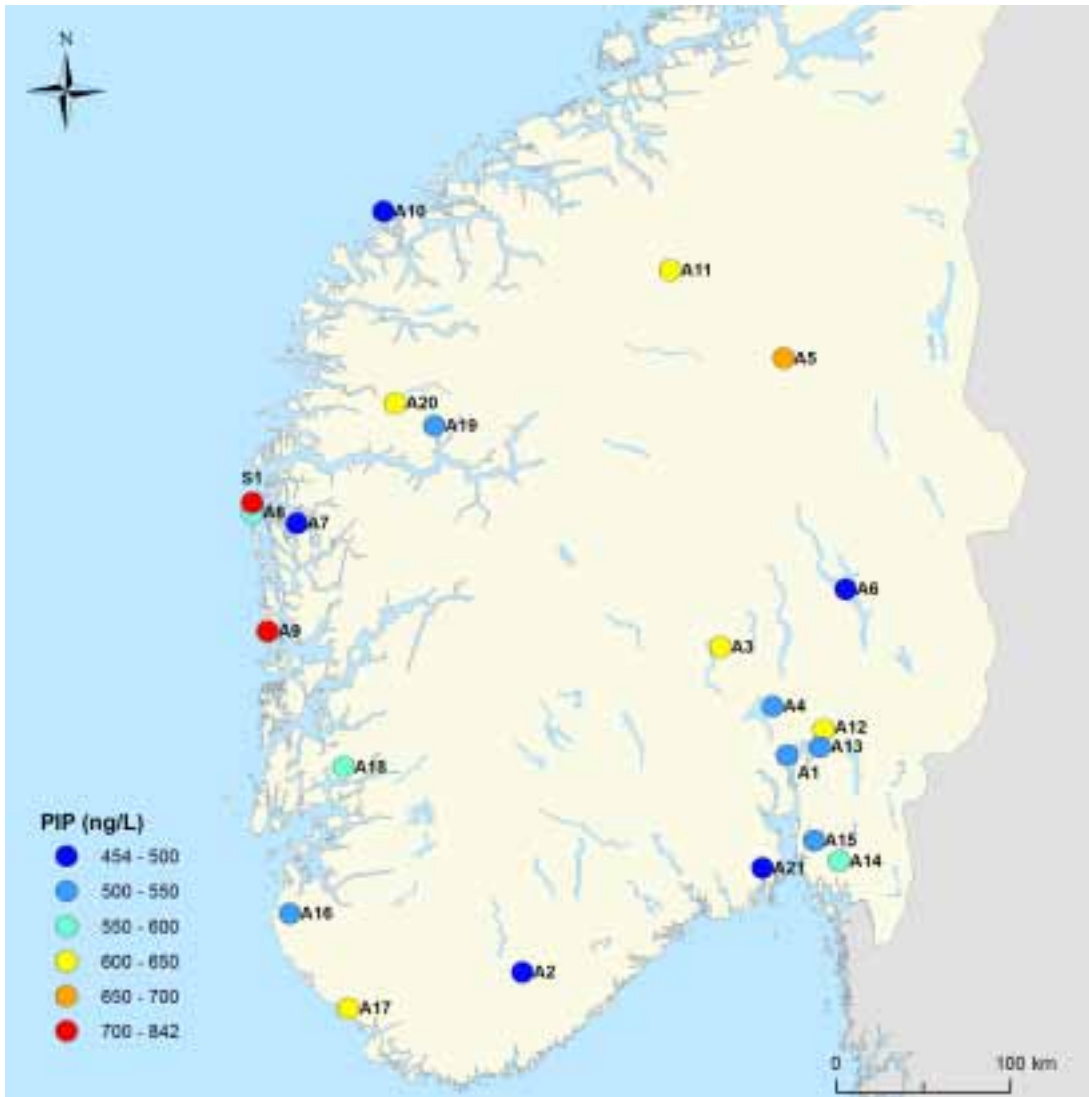


**Figure 10.** Concentrations of MA in the study lakes. MilliQ and tap water references had mean concentrations of 911 and 725 ng/L respectively.

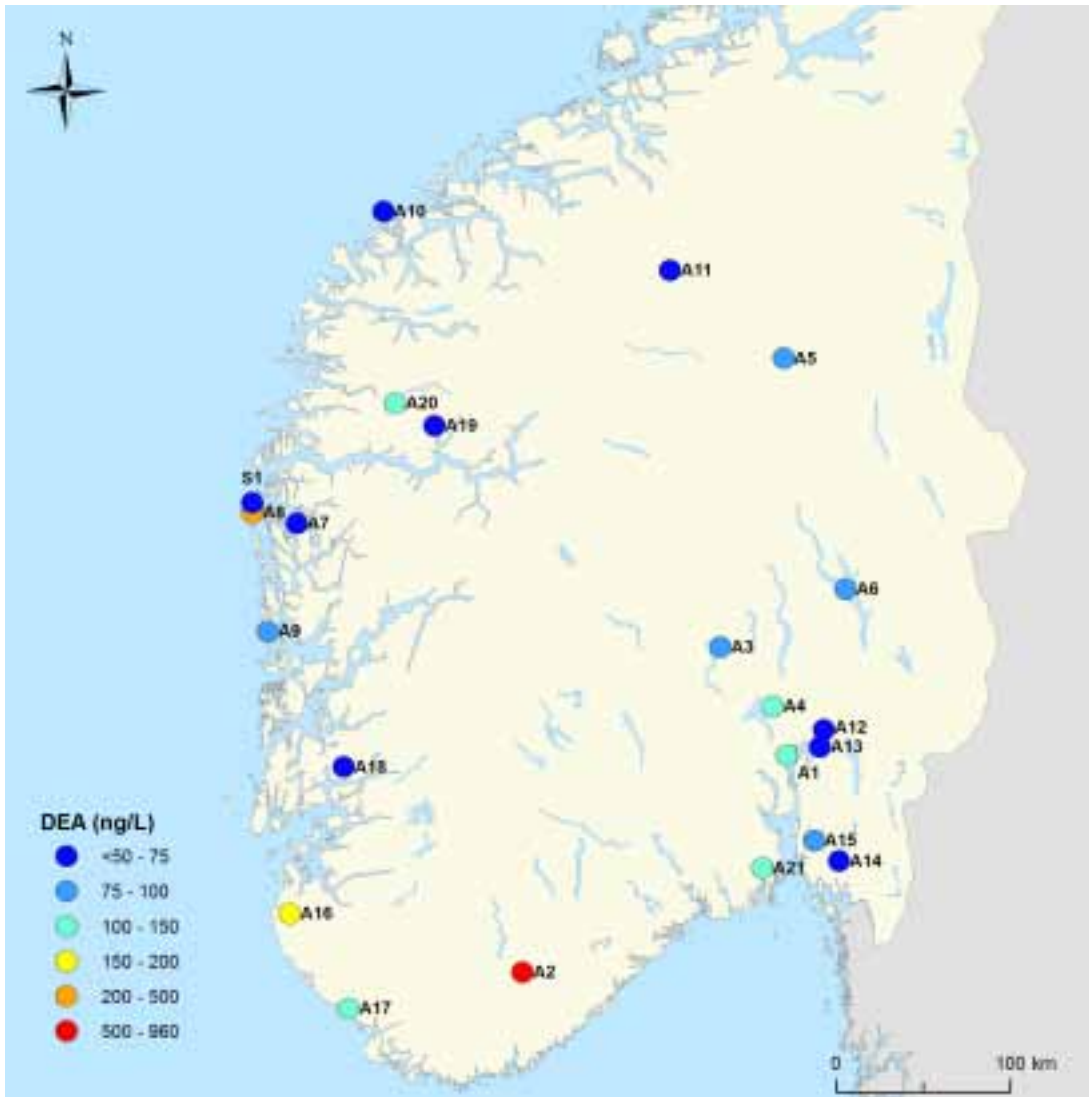


**Figure 11.** Concentrations of MEA in the study lakes. MilliQ and tap water references had mean concentrations of 993 and 1 048 ng/L respectively.





**Figure 12.** Concentrations of PIP in the study lakes. MilliQ and tap water references had mean concentrations of 589 and 712 ng/L respectively.



**Figure 13.** Concentrations of DEA in the study lakes. MilliQ and tap water references had mean concentrations of 98 and <50 ng/L respectively.

To our knowledge, with the exception of one study in a Chinese lake (Cai et al. 2003), and some source water samples from six reservoirs and one lake in China (Wang et al. 2011), the current study along with survey carried out by NIVA in 2011 (Grung et al. 2012) represents the only data available for amine concentrations in lakes. The concentrations of select amines found in Norwegian lakes (especially aliphatic amines) were generally high compared to the concentrations reported for other studies. For instance, Gerecke and Sedlak (2003) remark that DMA concentrations in municipal wastewaters often range from 2.3–22.5 µg/L, while for some of the natural freshwater lakes included in the NIVA survey, concentrations were comparable to the upper end of this reported range. Cai et al. (2003) also report high amine concentrations in water from a heavily polluted urban lake in China (i.e. 48 µg/L MA, 21 µg/L DMA and 70 µg/L EA). Meanwhile Wang et al. (2011) found amine concentrations in reservoirs ranging from 0.6–3.8 µg/L for DMA and concentrations of 0.3–2.4 µg/L for DEA; PIP was only detected in one reservoir (0.3 µg/L) and MEA was not detected in any samples. For the one lake sampled by Wang et al. (2011), DMA and MEA concentrations were both 0.2 µg/L, and DEA and PIP were not detected.

Three of the sites in the current study were also included in the 2011 NIVA survey in the Mongstad region: Fonnebostvatnet (A7; M11 in 2011 study), Langevatnet (A8; M16 in 2011 study) and Storavatnet (A9; M52 in 2011 study). For each of these sites, amine concentrations differed strongly between the 2011 and 2012 surveys (when data without blank subtraction is compared), suggesting a high degree of temporal variability in concentrations of these compounds. MA, DMA and DEA concentrations were consistently higher in 2011 than in 2012, while MEA and PIP concentrations were lower in 2011 than in 2012.

There were also substantial differences in water chemistry between the 2011 and 2012 sampling dates (e.g. TOC, TP and TN concentrations were consistently higher for the 2011 sampling date than for the current study). These are likely attributable to seasonal differences in both water chemistry and amine concentrations, since the 2011 samples were collected during autumn overturn, while the 2012 samples were collected during the summer. The higher TOC (and MA and DMA) concentrations in the autumn were likely due to inputs of TOC-rich water from the terrestrial catchment, possibly due to autumnal litterfall inputs of labile carbon to the catchment.

### 3.3.2 Correlations between amines and environmental parameters

We explored potential relationships between concentrations of the seven measured amines, and found that methylamine and dimethylamine concentrations were strongly positively correlated (Table 10). There are strong structural similarities between this pair of primary and secondary amines, and it is possible that this relationship reflects a common source for these two amines. There were no other significant correlations found between concentrations of the measured amines.

**Table 10.** Pearson's correlation coefficients (*r*) for correlations between concentrations of measured amines for freshwater samples. Correlations shown are significant at the  $P < 0.01$  level.

| Lake | MA   | EA | MEA | DMA | DEA | AMP | PIP |
|------|------|----|-----|-----|-----|-----|-----|
| MA   | 1    |    |     |     |     |     |     |
| EA   |      | 1  |     |     |     |     |     |
| MEA  |      |    | 1   |     |     |     |     |
| DMA  | 0.83 |    |     | 1   |     |     |     |
| DEA  |      |    |     |     | 1   |     |     |
| AMP  |      |    |     |     |     | 1   |     |

PIP

1

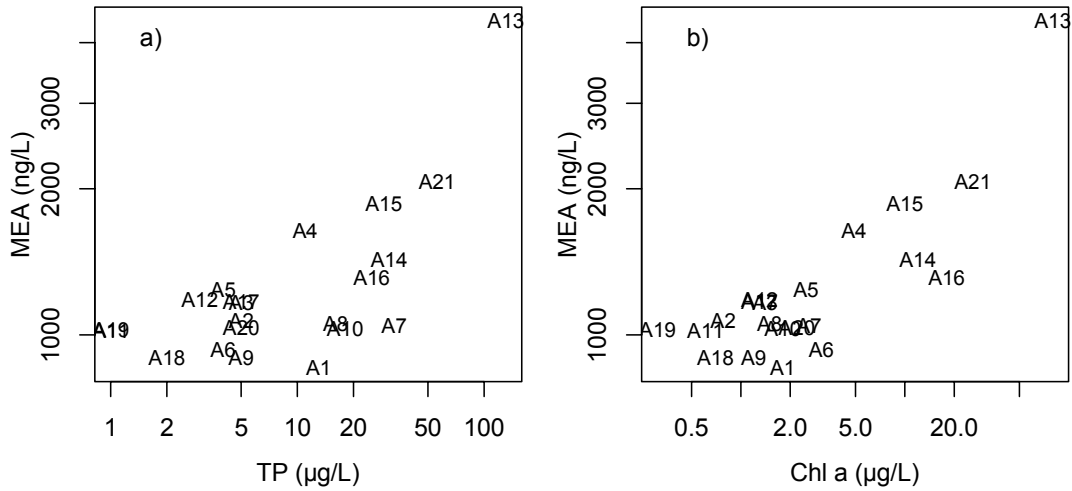
Finally, we sought to explore potential relationships (Table 11) between the concentrations of the seven measured amines and the water chemistry parameters included in the current study. These relationships were tested in order to gain insight into the factors that determine concentrations of amines in Norwegian freshwaters.

**Table 11.** Pearson's correlation coefficients ( $r$ ) for correlations between concentrations of measured amines and water chemistry parameters for freshwater samples. Correlations shown are significant at the  $P < 0.01$  level.

| Lake | pH    | TP   | TN    | NO <sub>3</sub> | TOC  | Na | Cl | SO <sub>4</sub> | Chl $a$ |
|------|-------|------|-------|-----------------|------|----|----|-----------------|---------|
| MA   | -0.56 |      |       |                 | 0.72 |    |    |                 |         |
| EA   |       |      |       |                 |      |    |    |                 |         |
| MEA  |       | 0.68 | 0.58  |                 |      |    |    |                 | 0.85    |
| DMA  |       |      |       |                 | 0.81 |    |    |                 |         |
| DEA  |       |      |       |                 |      |    |    |                 |         |
| AMP  |       |      |       |                 |      |    |    |                 |         |
| PIP  |       |      | -0.56 |                 |      |    |    |                 |         |

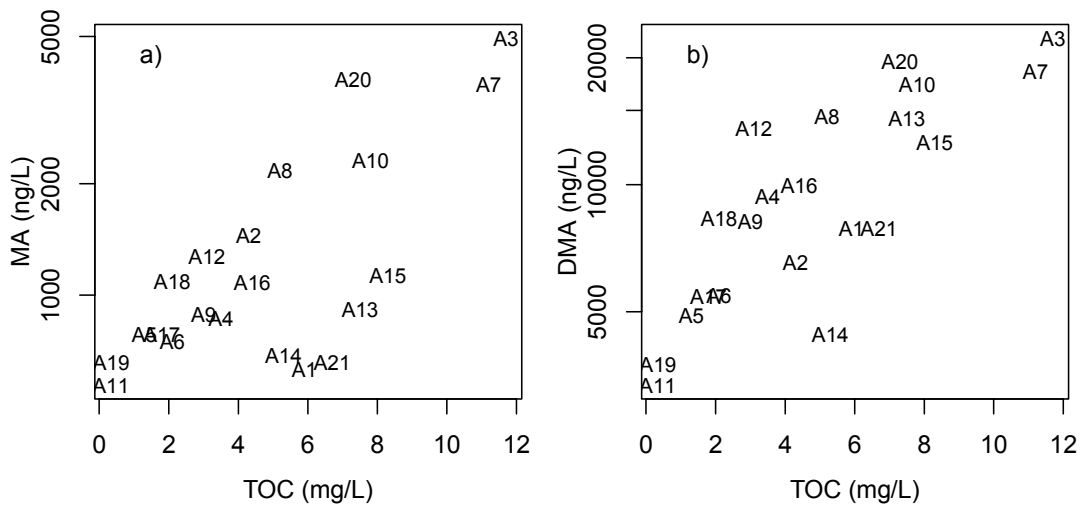
Two main observations emerged from these analyses: 1) monoethanolamine (MEA) concentrations were highest in eutrophic lakes (high nutrient and chlorophyll concentrations); and 2) methylamine (MA) and dimethylamine (DMA) were highest in humic lakes (high TOC and low pH).

Monoethanolamine (MEA) concentrations appeared to be related to lake trophic status, with lakes where nutrient concentrations and phytoplankton biomass (as indicated by chlorophyll  $a$ ) are high tending to have higher MEA concentrations (Figure 14). It is possible that MEA is being produced in the lake by phytoplankton, with higher phytoplankton biomass leading to higher MEA production. Alternatively, there may be an external source of MEA that is related to the factors that determine nutrient loading to a lake. However, the relationship between MEA and Chl  $a$  is much stronger than the relationships between MEA and either TN or TP concentrations (Table 11), supporting the possibility of in-lake production of MEA by phytoplankton. Furthermore, when comparing lakes with similar nutrient (TP and TN) concentrations, but different chlorophyll  $a$  concentrations (e.g. Tunevatnet (A14) vs. Fonnebostvatnet (A7)), the MEA concentrations tend to be highest where chlorophyll concentrations are higher.



**Figure 14.** Relationship between a) MEA and total phosphorus concentrations, and b) MEA and chlorophyll *a* concentrations. Correlation coefficients for these relationships are found in Table 11.

Meanwhile, the elevated MA and DMA concentrations in humic lakes (where TOC concentrations are high and pH is often low) suggest that these amines are primarily related to leaching of organic matter from the terrestrial catchment. The lakes with the highest MA and DMA concentrations tended to be lakes with extensive wetlands in their catchments, which can export a great deal of organic matter to lakes. The strong relationship between TOC and both MA and DMA (Figure 15) suggest that TOC concentrations could act as a useful predictor of concentrations of these aliphatic amines in freshwaters. This relationship may also explain the seasonal differences in concentrations of these amines between the 2011 (from the baseline survey) and 2012 sampling dates, where TOC (and subsequently MA and DMA) concentrations were higher in autumn of 2011 than in summer of 2012.



**Figure 15.** Relationship between a) MA and TOC concentrations, and b) DMA and TOC concentrations. Correlation coefficients for these relationships are found in Table 11.

### 3.3.3 Results after blank subtraction

As discussed in section 5.3.1, reference samples of both tap and MilliQ water were found to have relatively high concentrations of several amines, and as such, there is some uncertainty with respect to how these values affect our interpretation of the observed amine concentrations in lake samples. The results presented above are based on data from which reference values have not been subtracted, based on the assumption that the reference samples are not true blanks, and are not amine free. However, it is also possible that these elevated reference values reflect a methodological artefact, in which case it would be appropriate to treat the reference values as blanks, and subtract these values from all surface water results. Below, we present some of the main results and relationships based on lake data from which tap water reference values have been subtracted (MilliQ references were not used given the particularly high DMA concentrations observed in these samples).

Amine concentrations in lake water after blank subtraction were often not detectable (ND), and ranged from not detectable (ND)–13 529 for DMA, ND–4 035 for MA, ND–3 442 for MEA, ND–136 for PIP and ND–862 for DEA. Meanwhile, many of the significant relationships observed for non-blank subtracted data were still observed after blank subtraction. For example the relationships between DMA and MA ( $r = 0.85$ ,  $P < 0.01$ ), MA and TOC ( $r = 0.77$ ,  $P < 0.01$ ), DMA and TOC ( $r = 0.75$ ,  $P < 0.01$ ), MEA and TP ( $r = 0.60$ ,  $P < 0.05$ ), MEA and TN ( $r = 0.59$ ,  $P < 0.05$ ), and MEA and Chl  $a$  ( $r = 0.82$ ,  $P < 0.01$ ) were very similar between raw and reference corrected data (see Table 11 for original correlation coefficients). This suggests that our conclusions about potential sources of amines to Norwegian freshwaters, including the importance of terrestrial catchment sources of both MA and DMA and the importance of *in situ* production of MEA by phytoplankton are robust regardless of our interpretation of the tap and MilliQ water reference values.

## 4. Conclusions

The study lakes chosen for analysis of amine concentrations were a good representation of the diverse range of conditions that exist in Norwegian lakes in terms of their water chemistry, exposure to various human activities and catchment land cover. The lakes provided gradients in several parameters, including: pH, trophic status, impact of acidification, and amount of humic matter (TOC). These gradients were used to assess the factors that influence amine concentrations in Norwegian lakes.

Amine concentrations ranged from <40 ng/L to 22 247 ng/L, and differed strongly between the amines measured as well as between the study sites. DMA was the most prevalent amine, followed by MA and MEA. There were also detectable concentrations of both DEA and PIP, while EA and AMP were not detected. Although amine concentrations have rarely been reported for lakes, these values are high relative to other observations for river water, and our observed DMA concentrations approach observed values for municipal wastewater.

We found that MEA concentrations appeared to be related to lake trophic status, with higher MEA concentrations in lakes where nutrient and phytoplankton concentrations were also high. Our observations indicated that in situ production by phytoplankton could be an important source of MEA in Norwegian lakes. We also found that both MA and DMA concentrations were closely related to TOC concentrations. Lakes that had high TOC concentrations (and high inputs of humic matter from their terrestrial catchments) tended to have high MA and DMA concentrations, suggesting that terrestrial input of organic matter may be an important source of these aliphatic amines to Norwegian freshwaters. Overall, both natural (e.g. export from terrestrial catchment) and anthropogenic (e.g. human-driven eutrophication and high phytoplankton biomass) factors appear to play an important role in determining eventual amine concentrations in these lakes.

Despite the uncertainty surrounding the interpretation of MilliQ and tap water reference results, and subsequent data treatment, we found that regardless of the data treatment approach (i.e. whether or not reference values were subtracted from lake sample concentrations), the conclusions above regarding the factors that contribute to concentrations of select amines (such as DMA, MA and MEA) still hold true. Future work will focus on the analytical methods for determination of amine concentrations. In particular we would like to carry out an inter-lab comparison for analysis of amines in lake water and will continue to work with NILU to determine how best to interpret the analytical results in the current study.

Future work should also characterize seasonal changes in amine concentrations in Norwegian lakes, and assess the factors responsible for these changes. It would also be relevant to assess whether elevated amine concentrations in eutrophic (MEA) and humic (MA, DMA) lakes are related to increased incidence of related toxic compounds such as nitrosamines and nitramines. The high concentrations of the secondary amine DMA in these lakes are of particular interest, given that secondary amines are capable of nitrosamine and nitramine formation.

These results have provided important insight into some of the environmental and human factors that influence amine concentrations in lakes, and can inform future work in assessment of the importance and potential impact of future increases in amine loading to Norwegian lakes (e.g. due to amine-based CO<sub>2</sub> capture).

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## Appendix A. Abbreviations

|                 |                                            |
|-----------------|--------------------------------------------|
| AMP             | 2-amino-2-methyl-propanol                  |
| Chl <i>a</i>    | chlorophyll <i>a</i>                       |
| Cl              | chloride                                   |
| DEA             | diethylamine                               |
| DMA             | dimethylamine                              |
| EA              | ethylamine                                 |
| LOD             | limit of detection                         |
| MA              | methylamine                                |
| MEA             | (mono)ethanolamine                         |
| Na              | sodium                                     |
| NILU            | Norwegian Institute for Air Research       |
| NIVA            | Norwegian Institute for Water Research     |
| NO <sub>3</sub> | nitrate                                    |
| PIP             | piperazine                                 |
| SO <sub>4</sub> | sulphate                                   |
| TCM             | CO <sub>2</sub> Technology Centre Mongstad |
| TOC             | total organic carbon                       |
| TN              | total nitrogen                             |
| TP              | total phosphorus                           |

## Appendix B. Personnel

The following people at NIVA participated in the project:

- **Merete Grung**, PhD – environmental toxicologist. Dr. Grung is a senior scientist with over 20 years of experience in analytical chemistry, environmental chemistry and environmental toxicology. Acted as the project leader.
- **Richard Wright**, PhD – environmental chemist. Dr. Wright is a senior research scientist with over 35 years of experience in hydrochemical research, including field studies, catchment-scale experiments and modelling. Acted as a senior advisor and provided quality assurance for the project.
- **Amanda Poste**, PhD – limnologist. Co-ordinated and carried out fieldwork, preparations for laboratory analysis, data analysis and played a central role in writing progress and final reports.
- **Espen Lund**, MSc – ecologist. Created maps related to the project, and collected background physicochemical data for lake selection.
- **Linda Marie Skryseth**, MSc – ecotoxicologist. Assisted with field sampling.
- **Tomas Adler Blakseth**, MSc – chemist. Blakseth is the acting research leader for the section for chemical analysis at NIVA and, along with colleagues in the NIVA lab, carried out chemical analysis and provided final data for major chemical components and chlorophyll *a* concentrations.
- **Andrew Harvey**, BA – assisted with fieldwork, and took the photos included in this report.

Amine analysis was carried out by **Christian Dye** (PhD) at NILU. Dye is a chemist with expertise in analysis of amines, nitrosamines and nitramines.

## Appendix C. Timetable

| Activity                                      | 2012 |      |        |           |         |          |          |  |  |  |   |  |   |
|-----------------------------------------------|------|------|--------|-----------|---------|----------|----------|--|--|--|---|--|---|
|                                               | June | July | August | September | October | November | December |  |  |  |   |  |   |
| Site selection                                |      |      |        |           |         |          |          |  |  |  |   |  |   |
| <b>Milestone: Sites selected 30/06</b>        | x    |      |        |           |         |          |          |  |  |  |   |  |   |
| Fieldwork/sample collection                   |      |      |        |           |         |          |          |  |  |  |   |  |   |
| <b>Milestone: Fieldwork completed 24/08</b>   |      | x    | x      |           |         |          |          |  |  |  |   |  |   |
| Chemical analysis: amines, water chemistry    |      |      |        |           |         |          |          |  |  |  |   |  |   |
| <b>Milestone: Analyses completed 31/10</b>    |      |      |        | x         | x       |          |          |  |  |  |   |  |   |
| Data analysis:                                |      |      |        |           |         |          |          |  |  |  |   |  |   |
| <b>Milestone: Analyses completed 20/11</b>    |      |      |        |           | x       | x        |          |  |  |  | x |  |   |
| Reporting (draft)                             |      |      |        |           |         |          |          |  |  |  |   |  |   |
| <b>Milestone: Draft report submitted 5/12</b> |      |      |        |           | x       |          |          |  |  |  | x |  |   |
| Reporting (final)                             |      |      |        |           |         |          |          |  |  |  |   |  |   |
| <b>Milestone: Final report due 31/12</b>      |      |      |        |           |         |          |          |  |  |  |   |  | x |

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