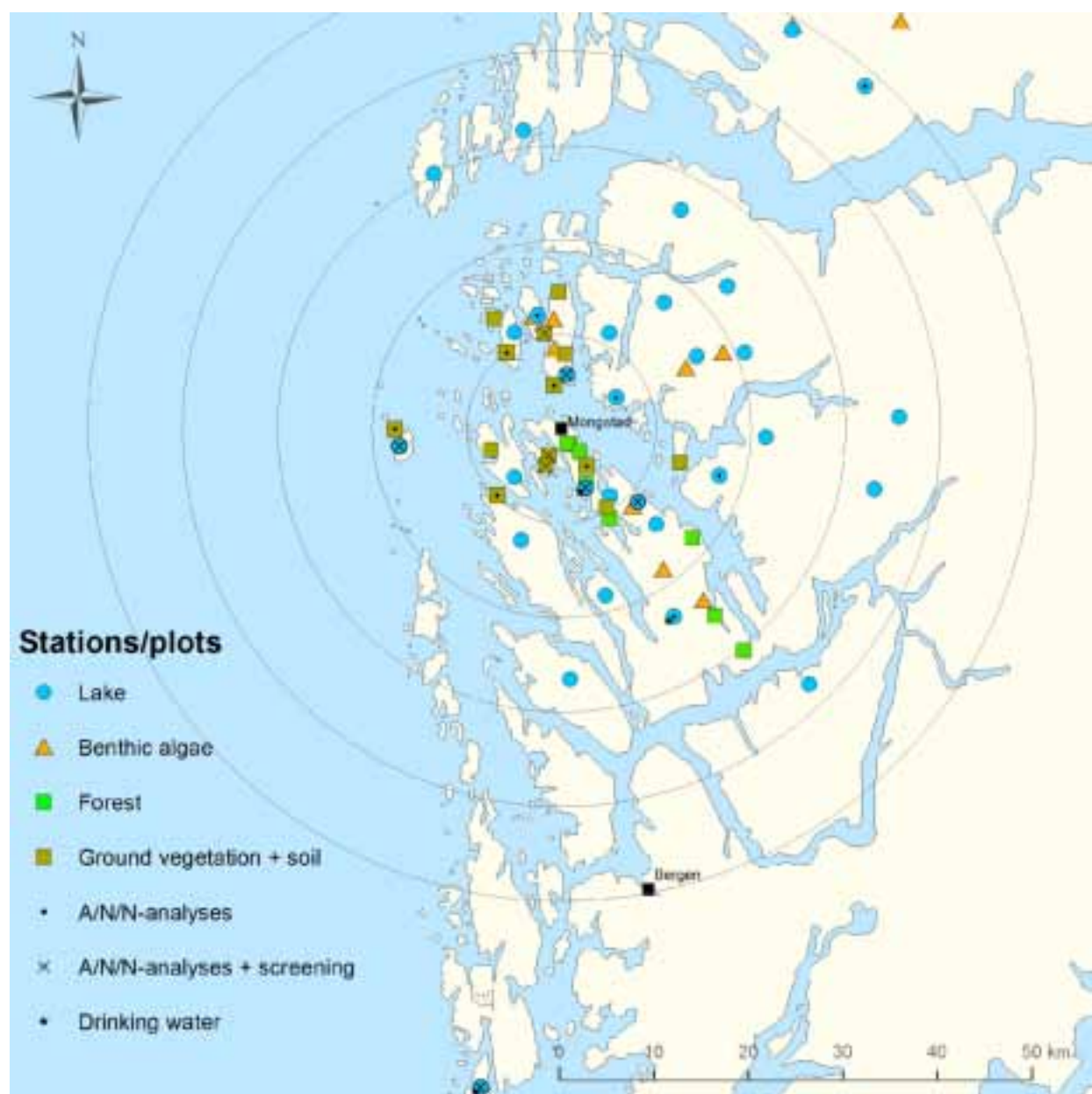




# Terrestrial and Aquatic Baseline Study and Monitoring Programme for CO2 Technology Centre Mongstad



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Title Terrestrial and Aquatic Baseline Study and Monitoring Programme for CO <sub>2</sub> Technology Centre Mongstad	Report No.. 6311-2012	Date 27/2-2012
	Project No. O-11183	Pages Price 98
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	Geographical area Mongstad	Printed NIVA

Client(s) CO <sub>2</sub> Technology Centre Mongstad DA	Client ref. Contract NO.: 4502184521
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**Abstract**

CO<sub>2</sub> Technology Centre Mongstad will be the world's largest test centre for testing and development of CO<sub>2</sub> capture technology. The emissions to the atmosphere from CO<sub>2</sub> Technology Centre Mongstad contain amines and may in addition contain or lead to the formation of degradation products from amine-based CO<sub>2</sub> capture technology. An environmental baseline survey was conducted in 2011 prior to the operation. The survey performed is broad, and describes in detail the environmental situation both in terrestrial and aquatic ecosystems as well as relevant chemical compositions of a range of matrices such as soil, plants and water. The data collected in the monitoring program were used to propose a future monitoring program in the area.

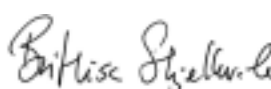
4 keywords, Norwegian 1. Tilstandsundersøkelse 2. CO <sub>2</sub> fangst 3. amin 4. naturmiljø	4 keywords, English 1. Baseline study 2. CO <sub>2</sub> capture 3. amine 4. environment
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**Terrestrial and Aquatic Baseline Study and  
Monitoring Programme for CO<sub>2</sub> Technology Centre  
Mongstad**

## **Addendum to report 6311-2012**

This report contains reported baseline levels of amines, nitrosamines and nitramines in addition to conventional analyses of water quality parameters such as pH, nitrate, phosphate etc. The levels of amines in aquatic environment are seldom reported, and the lack of available data on amines in surface waters is in part due to the analytical challenges associated with analysis of amines in complex environmental matrices.

The levels of amines have been investigated by us in subsequent projects aiming at identifying the main factors affecting the concentrations of these compounds (NIVA report 6781-2015). The analyses of amines in all NIVAs projects so far have been performed by NILU. During this subsequent project work, several iterations of the method for determining amines have been employed by NILU. Three major changes to the method employed for analysing amines have been the result of method development and a change of instrument. The latest analytical method (spring 2014) unfortunately indicates that the levels of amines reported in this baseline study may be hampered by the detection of artefacts. The latest knowledge therefore indicates that the high levels reported are therefore not correct (Table 5.3.5). For a detailed discussion of the problems associated with the analytical problems, we refer to the aforementioned report (NIVA report 6781-2015).

The levels of nitramines and nitrosamines have not been hampered by the analytical challenges associated with amines. In addition, the base-line levels were all below detection limits for these two groups of analytes.

## **Preface**

The baseline survey of terrestrial and aquatic environmental quality was conducted by NIVA (Norwegian Institute for Water Research) and NFLI (Norwegian Forest and Landscape Institute). The personell involved in the project are presented in Appendix 10.2, and all the persons are thanked for a thorough and well performed study.

The baseline study was performed on commission from CO2 Technology Centre Mongstad DA. We thank the people involved on behalf of TCM for constructive and enthusiastic discussions during the project – in particular Penny Nicolaisen, Gelein de Koeijer, Bjarne Nenseter and Sissel Nepstad.

NILU (Norwegian Institute for Air Research) carried out the analyses for amines, nitrosamines and nitramines. We thank Christian Dye for a good cooperation with the analytical work.

Oslo, February 2012

*Merete Grung*

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# 1. Summary

The emissions to the atmosphere from CO<sub>2</sub> Technology Centre Mongstad (hereafter: TCM) contain amines and may in addition contain or lead to the formation of degradation products from amine-based CO<sub>2</sub> capture technology such as nitrosamines and nitramines. The emitted compounds and degradation products may be toxic and/or carcinogenic. They may also contribute to nutrient imbalance (eutrophication) and acidification of ecosystems. Emissions to the atmosphere thus pose three separate environmental concerns. In order to evaluate the potentially toxic, eutrophying and acidifying effects of deposition of these compounds after start-up and operation of TCM, a baseline survey was conducted in 2011 prior to the operation at TCM.

The baseline survey was designed to collect pre-operation data against which environmental effects of emissions from operation of TCM can be evaluated. The key questions are

- whether the concentration of amines, nitramines and/or nitrosamines or other potentially harmful substances in the environment will exceed recommended guideline values for organisms or humans (drinking water)
- whether the emissions lead to nutrient imbalance, acidification, altered production and/or changed biodiversity of organisms in terrestrial and aquatic ecosystems

Sensitive species and receptors were selected to monitor the possible environmental effects of the emissions. Reported air dispersion calculations were used to define the area that was covered. The baseline study covered aquatic and terrestrial locations in the area potentially affected by the emissions.

With respect to the possible eutrophying effect of enhanced nitrogen deposition in terrestrial ecosystems, the following receptors were chosen: ground vegetation, mosses (bryophytes) and lichens, trees and soils. In the aquatic ecosystems, lake water and benthic algae were selected as receptors for possible effects of eutrophication and acidification.

With respect to the potentially toxic effect of the compounds, concentrations of several amines, nitramines and nitrosamines were measured in soils, plants and water. Sensitive chemical analysis was utilised, with detection limits lower than the recommended guideline values for drinking water and/or the toxicity limits for the compounds. In addition, an analytical screening for unknown chemicals with functional groups of amine, nitramine or nitrosamine origin was performed on a subset of samples of plants, soil and water samples.

The species composition and distribution of the *Calluna* dominated heaths investigated suggest that the vegetation in general is associated with low nitrogen availability. Critical loads for transitions of heathlands into more grass-dominated vegetation in Norway are in the range of 10 to 20 kg N ha<sup>-1</sup> yr<sup>-1</sup>, and since the background deposition level in the Mongstad area is 8 to 13 kg N ha<sup>-1</sup> yr<sup>-1</sup>, the critical loads are at least partly exceeded. Thus, additional N will speed up the process in which abundance and composition of species move towards a higher dominance of grass species.

It is nevertheless questionable whether the terrestrial eutrophication indicators will be sufficiently sensitive to respond to the expected additional N deposition of about 0.03 kg N ha<sup>-1</sup> yr<sup>-1</sup> (c. 0.3% increase). However, if the worst case scenario applies (0.7 kg N ha<sup>-1</sup> yr<sup>-1</sup>), slow and gradual changes in the heathlands, growth rate of pine and algae on birch stems may occur. It is questionable whether the high emission scenario will be statistically reflected in the tissue N concentration of heather, *Cladonia* and *Hylocomium*, due to the flat response curves to increased N supply in these species.



With regards to the benthic algae, all three sites north of Mongstad were oligotrophic and slightly acidic, and as such are directly comparable with the reference sites in Flekke-Guddal and Yndesdal. In contrast, agricultural use and probably a slightly different geology lead to more eutrophic and less acidic streams in the area south of Mongstad. One of the suggested sites south of Mongstad, however, is oligotrophic. Nitrogen emissions from TCM could lead to increased algae biomass at this site, such that regular monitoring at this site is highly relevant.

The water chemistry with regards to eutrophication and acidification parameters was classified according to the EU Water Framework Directive where possible. The results show that the monitoring programme encompassed a combination of acid sensitive, eutrophic, and pristine surface waters. Some lakes had elevated concentrations of total nitrogen and total phosphorus, and did not achieve "good status" according to the Water Framework Directive classification. The levels in most of the lakes can most likely be ascribed to runoff from farming activities.

Increased emissions and deposition of nitrogen can lead to acidification of surface water. Acid neutralising capacity is a measure of the acidification status of water. Several of the lakes investigated were acidified by this measure as they had low acid neutralising capacity. In all these lakes, except one, low pH and reduced alkalinity were measured as well, indicating that the lakes were sensitive to acid deposition. Chemical analyses from the remaining lakes indicated that these were less sensitive to acidification. They are located in pristine areas with minor human pressure. Levels of total organic compounds and pH varied between the lakes, mainly due to influence of humic material, representing lakes of oligotrophic and dystrophic character.

In addition to eutrophication parameters, selected samples were also analysed for a range of amines, nitramines and nitrosamines. Hence, ten water samples and eight plant and soil samples were analysed for 7 amines, 5 nitramines and 9 nitrosamines. Samples that according to models of the deposition would receive the highest load were chosen for analysis. The level of detection for the compounds was in the  $\text{ng L}^{-1}$  and  $\text{ng g}^{-1}$  or lower for all compounds.

None of the nitramines or nitrosamines was detected above the detection limit in any of the samples investigated. However, all the amines investigated, except piperazine, were detected in all the matrices investigated. The levels ranged from low  $\text{ng g}^{-1}$  to almost  $\mu\text{g g}^{-1}$  in plant and soil samples, while the levels in water was from  $10 \text{ ng L}^{-1}$  to  $50 \mu\text{g L}^{-1}$  in water depending on the amine. The amine observed in highest levels in all matrices was dimethylamine, which is a natural constituent of many plants. The level of dimethylamine and methylamine in water was correlated with the total organic carbon level. The levels of amines detected in moss and soil seem to be in line with what has been reported in the literature. The majority of amines detected can be a result of natural sources, but anthropogenic sources can also be a possibility.

In addition to the target chemical analyses performed, a broad chemical screening by gas chromatography time of flight mass spectrometry and liquid chromatography quadrupole mass spectrometry has been performed. The data have been saved for later comparison. An aliquot of all the matrices sampled in this study has been stored, and will be kept at  $-20 \text{ }^\circ\text{C}$  for a period of 5 years.

A simple and initial environmental risk assessment show that the levels of amines, nitramines and nitrosamines that were previously assigned a predicted no effect concentrations were far below this value. The detection level of nitramines and nitrosamines are also below the recommended tolerable drinking water concentration for these compounds.

Based on the scientific results in this report, a future monitoring program has been proposed.

## 2. Norsk sammendrag

Utslipp til atmosfæren fra CO<sub>2</sub> Technology Centre Mongstad (TCM) inneholder aminer, og kan i tillegg inneholde omdanningsprodukter som nitraminer og eller nitrosaminer. De to sistnevnte grupper av forbindelser kan være toksisk og/eller karsinogene. Utslippene kan også føre til forhøyet næringstilgang (eutrofiering) og eventuelt forsuring av økosystemene. Dette betyr at utslippene potensielt kan medføre tre ulike påvirkninger på miljøet. For å kunne vurdere disse tre påvirkningene på miljøet etter oppstart av TCM, ble det gjennomført en tilstandsundersøkelse i 2011 før oppstart av TCM.

Tilstandsundersøkelsen var utformet slik at eventuelle påvirkninger på miljøet lett kan fanges opp etter oppstart av TCM.

Områdene det ble fokusert på er:

- om aminer, nitraminer eller nitrosaminer eller andre potensielt miljøfarlige komponenter forekommer i konsentrasjoner som overstiger anbefalte grenseverdier for mennesker (i drikkevann) eller vannlevende organismer
- om utslipp fører til forhøyet næringstilgang, forsuring, forandret produksjon eller endret biodiversitet av organismer i terrestrisk eller akvatisk økosystem

Det ble valgt følsomme arter og markører for å være i stand til å overvåke en eventuell miljøpåvirkning av utslippene. Modellberegninger av utlippenes geografiske omfang ble brukt for å bestemme lokalisering av de ulike undersøkelsene. Tilstandsundersøkelsen dekker terrestriske og akvatiske lokaliteter i det området som potensielt vil berøres av utslippene.

For å beskrive tilstanden med hensyn til eutrofiering, som er en følge av økt nitrogenavsetning, ble følgende terrestriske markører valgt: vegetasjonsanalyser, mose, lav, trær og jord. For akvatisk miljø ble overflatevann og påvekstvalger valgt som indikatorer for mulige effekter av økt næringstilgang og forsuring.

Når det gjelder den mulige toksiske virkningen av utslippene, ble konsentrasjonen av flere aminer, nitraminer og nitrosaminer målt i jord, mose og overflatevann. Det ble benyttet svært følsomme kjemiske analyser, med deteksjonsgrenser som er lavere enn den anbefalte grenseverdien for drikkevann og grenseverdien for vannlevende organismer. I tillegg ble det gjennomført en kjemisk screening på utvalgte prøver.

I det undersøkte studieområdet ser vi at røsslyng-dominert lynghei har en artssammensetning og utbredelse som er assosiert med liten tilgang på nitrogen. Tidligere studier har vist at lyngheier endres til mer gressdominert vegetasjon når nitrogendeposisjonen overskrider 10 to 20 kg N ha<sup>-1</sup> yr<sup>-1</sup>. Bakgrunnsdeposisjonen i Mongstadorrådet er 8 to 13 kg N ha<sup>-1</sup> yr<sup>-1</sup>, noe som betyr at dagens deposisjon allerede er innenfor intervallet for tålegrensen. Vi antar derfor at en ytterligere tilførsel av nitrogen vil påskynde en utvikling der lyngheiene blir mer gressdominert.

Det er imidlertid tvilsomt om de terrestriske eutrofieringsindikatorene er tilstrekkelig følsomme til å respondere en modellert forventet økning av nitrogen fra TCM på rundt 0.03 kg N ha<sup>-1</sup> yr<sup>-1</sup> (c. 0.3%). Hvis det verst tenkelige scenariet skulle slå til (0.7 kg N ha<sup>-1</sup> yr<sup>-1</sup>), kan vi derimot forvente en sakte og gradvis endring i artssammensetningen til lyngheiene, samt økt tilvekst av furu og tiltakende algevekst på bjørkestammer i berørte områder. Det er mer usikkert om dette scenariet kan føre til økt N-konsentrasjon i røsslyng, reinlav og etasjehusmose.

Når det gjelder påvekstalger, viste analysene at de tre stasjonene nord for Fensfjorden var oligotrofe og svakt forsuret. De er dermed direkte sammenlignbare med referansestasjonene i Flekke-Guddal og Yndelsdal. Stasjonene sør for Mongstad var derimot annerledes, antagelig som en funksjon av jordbruk og ulik geologi som fører til mer eutrofiering og mindre forsuring. En av stasjonene sør for Mongstad var imidlertid oligotrof. Nitrogenavsetning fra TCM kan føre til økt biomasse av alger på denne stasjonen, slik at overvåkning av påvekstalger er høyst relevant.

Vannkjemien i innsjøene ble klassifisert med hensyn til eutrofierings- og forsuringsparametere etter EUs rammedirektiv for vann der det var mulig. Resultatene viser at de valgte innsjøene inkluderer en kombinasjon av syrefølsomme, eutrofe og uberørte overflatevann. Noen av innsjøene hadde økte konsentrasjoner av nitrogen og fosfor, og oppnådde ikke «god» status i henhold til EUs rammedirektiv for vann. De forhøyede nivåene av næringsstoffer i innsjøene kan mest sannsynlig tilskrives utlekking fra jordbruk.

Økt utslipp og deponering av nitrogen kan føre til forsuring av overflatevann.

Syrenøytraliseringskapasitet er en mal på forsuringstilstanden i vannet. Flere av innsjøene som ble undersøkt var forsuret. Disse innsjøene, utenom en, hadde også lav pH og alkalinitet. Dette indikerer at innsjøene er følsomme for syreavsetning. Resten av innsjøene var mindre følsomme, og de befant seg i uberørte områder med lite bosetning. Nivåer av organisk karbon og pH varierte mellom innsjøene, stort sett som en funksjon av humusmateriale, og viser innsjøer av oligotrof og dystrof karakter.

Utvalgte prøver ble analysert for en rekke aminer, nitraminer og nitrosaminer. I alt ble ti vannprøver, åtte moseprøver og åtte jordprøver analysert for til sammen syv aminer, fem nitraminer og ni nitrosaminer. Prøvene som ble valgt for disse analysene var de som i følge modellberegninger ville være utsatt for høyest avsetning. Deteksjonsgrensen for analysene var i  $\text{ng L}^{-1}$  og  $\text{ng g}^{-1}$  eller lavere for alle forbindelsene.

Ingen av de undersøkte nitraminene eller nitrosaminene ble påvist i noen av de analyserte prøvene. På den annen side ble alle aminene (unntatt piperazin) påvist i alle prøvematrikser. Nivåene varierte fra lavt  $\text{ng g}^{-1}$  til nesten  $\mu\text{g g}^{-1}$  i planter og jord, mens nivået i vann var på  $10 \text{ ng L}^{-1}$  til  $50 \mu\text{g L}^{-1}$  i vann, avhengig av amin. Aminet som ble påvist i høyest konsentrasjon i alle matrikser var dimetylammin. Dette aminet er vist å være en naturlig bestanddel i blant annet planter og alger. Nivået av dimetylammin og metylamin i vann korrelerte med innholdet av organisk karbon. Nivået av aminer i mose og jord ser ut til å være sammenlignbart med hva som er funnet tidligere, mens nivået i vann synes å være høyere enn tidligere rapportert. Mange av aminene som ble påvist kan være et resultat av naturlige kilder, men menneskeskapt kilder kan ikke utelukkes.

I tillegg til målrettede analytiske målinger, ble det gjennomført en analytisk screening ved bruk av gasskromatografi med høyoppløselig massespektrometrisk deteksjon samt væskechromatografi med kvadrupol massespektrometrisk deteksjon. Dataene fra screeningen er lagret for eventuell senere sammenligning. En alikvot av alle prøver har blitt lagret ved  $-20 \text{ }^\circ\text{C}$ , og vil bli lagret i fem år.

Det ble foretatt en enkel risikovurdering basert på tidligere toksisitetsstudier for de forbindelsene der det var mulig. Risikovurderingen for dette utvalget av forbindelser viste at nivåene er langt lavere enn rapporterte grenseverdier for akvatiske organismer. Deteksjonsgrensen for nitraminer og nitrosaminer er også lavere enn den anbefalte grenseverdien for drikkevann.

Basert på de vitenskapelige resultatene i tilstandsundersøkelsen er det foreslått et fremtidig overvåkningsprogram.

### 3. Introduction

CO<sub>2</sub> Technology Centre Mongstad (hereafter: TCM) will be the world's largest test centre for testing and development of CO<sub>2</sub> capture technology. The emissions to the atmosphere from TCM contain amines and may in addition contain or lead to the formation of degradation products from amine-based CO<sub>2</sub> capture technology such as nitrosamines and nitramines. The emitted compounds and degradation products may be toxic and/or carcinogenic. They may also contribute to nutrient imbalance (eutrophication) and acidification of ecosystems. Emissions to the atmosphere thus pose three separate environmental concerns. In order to evaluate the potentially toxic, eutrophying and acidifying effects of deposition of these compounds after start-up and operation of TCM, a baseline survey was conducted in 2011 prior to the operation at TCM.

The baseline survey was designed to collect pre-operation data against which environmental effects of emissions from operation of TCM can be evaluated. The key questions are

- whether the concentration of amines, nitramines and/or nitrosamines or other potentially harmful substances in the environment will exceed recommended guideline values for organisms or humans (drinking water)
- whether the emissions lead to nutrient imbalance, acidification, altered production and/or changed biodiversity of organisms in terrestrial and aquatic ecosystems

Sensitive species and receptors were selected to monitor the possible environmental effects of the emissions. Reported air dispersion calculations (Berglen et al. 2010, Tønnesen 2011) were used to define the area that was covered. The baseline study covered aquatic and terrestrial locations in the area potentially affected by the emissions. Many of the aquatic sites have been previously used in conjunction with evaluation of potential environmental effects of the refinery at Mongstad (Traaen and Henriksen 1989, 1990, 1991, 1992). Baseline studies on air and deposition quality have been conducted in parallel by NILU (Tønnesen et al. 2011).

## 4. Materials and methods

### 4.1 Site selection

#### 4.1.1 Terrestrial site selection

Increased biomass of some grasses and decline of sensitive herbs, mosses and lichens may be expected from increased N supply (Aarrestad et al., 2010). Monitoring programs have shown that N deposition can increase N, P and K contents in heather (Edmondson et al., 2010). Our approach was designed to establish a baseline against which future changes can be detected. The surveys for assessment of species richness and abundance were, as far as possible, established in a subset of the catchments of the sites used for water sampling. A total of 14 sites within a distance of about 40 km from Mongstad were established, 6 to the north of Mongstad/ Fensfjorden, and 8 sites to the east and south of Mongstad. According to air pollution distribution models (Berglen et al. 2010) the emissions from Mongstad will be spread predominantly along a NNW – SSE axis, and a considerable gradient in air pollution load is expected over the sites with this sampling design.

Species composition is a sensitive indicator of eutrophication (nutrient enrichment) of ground vegetation (Aarrestad et al., 2010). Ground vegetation is defined here as all plant species and lichens other than trees. Heather moorland ecosystems are especially vulnerable due to the low nitrogen (N) status of these ecosystems, and in large areas of southern Norway the critical load of N deposition is exceeded by the present N deposition (Aarrestad et al., 2010; Edmondson et al. 2010). Most of the study area around Mongstad has been under continuous management for centuries and is characterised by a diversity of different successional vegetation stages. Traditional coastal farming including mowing, rotational burning and sod cutting has resulted in various semi-natural habitats (Måren and Vandvik 2009). Due to this historical use forest cover is modest, particularly to the west and north of Mongstad. In the southern part, however, forests are more widespread. This has been taken into account in the spatial distribution of sites. Two sets of terrestrial sites were established:

1) Ground vegetation. Sites for assessment of richness and abundance of the ground vegetation in non-forested areas. Important selection criteria for the vegetation sites were:

- To represent the future gradient in deposition - sites were selected both upwind (to the west, relatively unaffected by emissions at Mongstad) and downwind (to the south, potentially affected by emissions at Mongstad)
- Nutrient-poor conditions - it is easier to detect eutrophication effects in nutrient-poor vegetation types
- Similar vegetation types - standardisation facilitates comparison between different sites
- Openness - to avoid the influence of forest cover on the ground vegetation
- Proximity to the lakes/watercourses that will be included in the aquatic study – to facilitate integration of the terrestrial and aquatic components.

2) Forest sites. Growth of pine was assessed on sites the south of Mongstad. The sites were distributed in a pollution gradient (cf. Berglen et al. 2010) and confined to forests with similar vegetation types to be able to detect possible eutrophication effects from TCM.

**Table 4.1.1** Location of the ground vegetation plots. County codes: H Hordaland; SF Sogn and Fjordane.

<i>Site</i>	<i>Municipality</i>	<i>County</i>	<i>Altitude (m)</i>	<i>Latitude</i>	<i>Longitude</i>
G1	Gulen	SF	1	60.895621	4.95682
G2	Lindås	H	7	60.782176	5.001444
G3	Austrheim	H	38	60.772041	4.998315
G4	Lindås	H	41	60.776874	5.076026
G5	Lindås	H	28	60.740995	5.126887
G6	Radøy	H	19	60.736763	4.913385
G7	Austrheim	H	40	60.778599	4.888249
G8	Fedje	H	9	60.783798	4.698124
G9	Gulen	SF	20	60.871916	4.889346
G10	Gulen	SF	17	60.90284	4.856491
G11	Gulen	SF	22	60.848033	4.989651
G12	Gulen	SF	136	60.880076	5.001818
G13	Gulen	SF	67	60.936726	4.971611

**Table 4.1.2** Location of the forest sites. County codes: H Hordaland; SF Sogn and Fjordane.

<i>Plot</i>	<i>Municipality</i>	<i>County</i>	<i>Altitude (m)</i>	<i>Latitude</i>	<i>Longitude</i>
F1	Austrheim	H	60	60.795201	5.039862
F2	Austrheim	H	100	60.795528	5.032979
F3	Lindås	H	67	60.789463	5.060213
F4	Lindås	H	45	60.761049	5.081416
F5	Lindås	H	13	60.731616	5.137674
F6	Lindås	H	50	60.724795	5.300062
F7	Lindås	H	25	60.654462	5.365251
F8	Lindås	H	105	60.625706	5.430798

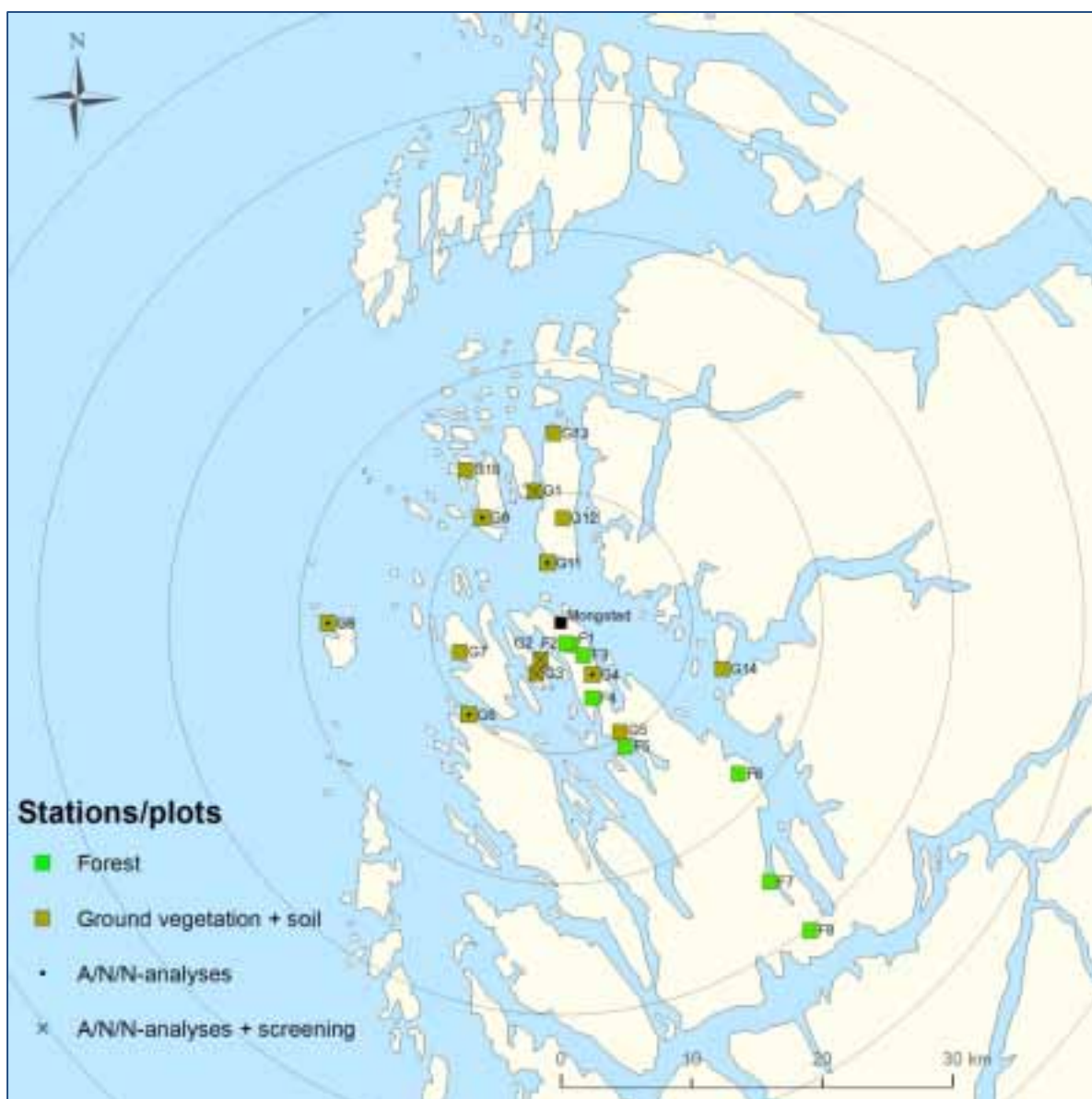


Figure 4.1.1 Map of the Mongstad area showing the ground vegetation (G) and forest sites (F).

#### 4.1.2 Aquatic station selection

##### *Benthic algae*

Benthic algae (periphyton) are very sensitive to both eutrophication and acidification, and thus are regularly used for biomonitoring purposes. They are autotrophic primary producers, i.e. they are photosynthesizing, and live at or near a river bottom. Benthic algae are among the first to react to environmental changes in water, and therefore they are also expected to be among the first organisms to react to eventual impacts of TCM. Benthic algae are stationary and cannot escape short time events by drifting with the current. Therefore, they will react to short time events which often are overlooked by chemical measurements.

NIVA has developed a sensitive and effective method for biomonitoring of ecological status in rivers based on species composition of benthic algae. Eutrophication impacts are detected by the PIT index (periphyton index of trophic status) (Schneider and Lindstrøm 2011), while river acidity is indicated by the AIP index (acidification index periphyton) (Schneider and Lindstrøm 2009).

Ten sites, six new and four previously-studied (Directorate for Nature Protection 2010, 2011), were selected for monitoring of benthic algae and included in this baseline study. Of the four previously-studied sites, two are in the Flekke-Guddal catchment north of Mongstad, an area expected to receive N deposition originating from Mongstad, and two are located in the Yndesdal catchment, an area not expected to receive N deposition originating from Mongstad. The six new sites are located in areas expected to receive N deposition from Mongstad. Three are located on the islands north of Mongstad, and three are located south of Mongstad. NIVA has data from previous studies on benthic algae species composition and abundance from the sites located in the Flekke-Guddal (Directorate for Nature Protection 2010) and Yndesdal catchments (Directorate for Nature Protection 2011). The sites closer to Mongstad were sampled for the first time in this baseline study.



**Figure 4.1.2** Map of the Mongstad area showing the location of the benthic algae stations.



**Table 4.1.3** Location and description of benthic algae stations

<i>Code</i>	<i>Site code</i>	<i>Catchment/location</i>	<i>Description</i>	<i>Latitude</i>	<i>Longitude</i>
B1	LSA MJØ	North of Mongstad	Mjømna	60.9095	4.9293
B2	LSA ÅNN	North of Mongstad	Ånneland	60.8831	4.9802
B3	LSA RAM	North of Mongstad	Outlet Randals- and Midtbøvatnet	60.9105	4.9688
B4	LLI ISK	South of Mongstad	Inlet Skodvensvatnet	60.6912	5.2524
B5	LLI DAL	South of Mongstad	Creek close to Dalsgrend	60.6675	5.3382
B6	LLI IFO	South of Mongstad	Inlet Fonnebostvatnet	60.7462	5.1744
B7	LDY BOT	Yndesdal	Botnanebekken	60.9035	5.3042
B8	LDY MAR	Yndesdal	Outlet Markhusdalsvatnet	60.8838	5.2374
B9	MGU MAR	Flekk-Guddal	Outlet Markhusvatnet	61.2203	5.3445
B10	MGU GUD	Flekk-Guddal	Guddal church, upstream lime dosing	61.2392	5.5535

### **Water chemistry**

Lakes rather than streams were selected as lakes are less sensitive to short-term temporal variations in deposition.

The following aspects were considered in the selection of the lakes:

- The lakes should cover the area that is expected to receive the highest deposition from Mongstad, as well as areas not expected to receive deposition from Mongstad
- The lakes should be sensitive, i.e. vulnerable to increasing contamination

Reported air dispersion calculations (Berglen et al. 2010; Tønnesen 2011) were used to define the area that was covered. Candidates were selected from the 39 lakes that were investigated during the acid rain monitoring programme of 1988-1991 (Traaen and Henriksen, 1988-1992). For the baseline study, 30 lakes, including two reference lakes outside the area affected by emissions from the TCM, were included. Among the chosen lakes, 3 were drinking water sources.

All 30 lakes were sampled for determination of concentrations of major ions and nutrients. A subset of 10 lakes was in addition sampled for determination of amines, nitrosamines and nitramines (A/N/N). Three of these are raw water sources for drinking water. Finally 5 of the 10 lakes were selected for chemical screening.

**Table 4.1.4** Lake information and location. County codes: H Hordaland; SF Sogn and Fjordane. NVEnr is the national identification number for lakes in the Norwegian Water Resources and Energy Directorate's (NVE) database.

<i>Code</i>	<i>Lake name</i>	<i>Municipality</i>	<i>County</i>	<i>Lake area (km<sup>2</sup>)</i>	<i>Altitude (m)</i>	<i>Latitude</i>	<i>Longitude</i>	<i>NVEnr</i>
M01	Nykksvatn	Gulen	SF	0.03	97	60.8924	4.8976	25993
M02	Kvernhusvatn	Gulen	SF	0.01	33	60.8599	5.0114	175749
M03	Svardalsvatn	Gulen	SF	0.80	29	60.9054	5.0811	25912
M05	Tjukketlavatnet	Lindås	H	0.16	10	60.7525	5.1306	26228
M06	Førlandsvatnet	Austrheim	H	0.06	12	60.7564	4.9410	26217
M08	Mjømnevatn	Gulen	SF	0.13	21	60.9112	4.9372	25939
M09	Norddalsvatn	Gulen	SF	0.03	102	60.9419	5.1769	25867
M10B	Markhusdalsvatnet	Masfjorden	H	0.25	96	60.8960	5.2557	26000
M11	Fonnebostvatnet	Lindås	H	0.06	23	60.7505	5.1846	26234
M12	Austrevatn v/Fjellsende	Lindås	H	0.24	11	60.7324	5.2267	26255
M13	Festevatn	Lindås	H	0.18	10	60.6583	5.1507	26334
M14	Færevatnet	Radøy	H	0.16	19	60.6984	4.9733	26283
M16	Langevatnet	Fedje	H	0.05	16	60.7681	4.7119	26190
M17	Gardavatn	Solund	SF	0.07	33	61.0292	4.6944	28922
M18	Nordre Nordgulvatnet	Gulen	SF	0.14	133	61.0313	5.1823	28939
M19	Klyvtveitvatnet	Gulen	SF	0.49	410	60.9661	5.2940	25807
M20	Grønefjellvatnet	Masfjorden	H	0.30	403	60.9064	5.3467	25980
M21	Storevatnet26130	Masfjorden	H	0.11	135	60.8298	5.4118	26130
M24	Storavatnet2059	Meland	H	3.14	10	60.5750	5.1070	2059
M26	Storevatnet28876	Solund	SF	0.19	29	61.0832	4.8539	28876
M28	Litlematrestøylvatnet	Masfjorden	H	0.26	611	60.8665	5.6628	26078
M29	Botnavatnet	Lindås	H	0.31	347	60.7955	5.6352	26183
M31	Kleppsvatnet	Osterøy	H	0.38	35	60.6030	5.5639	26389
M32	Markhusvatnet	Hyllestad	SF	1.43	214	61.2160	5.3460	1640
M33B	Sørestrandsvatnet	Høyanger	SF	0.67	238	61.1730	5.5039	1627
M50	Rotevatnet	Lindås	H	0.07	34	60.7543	5.0824	26224
M51	Storavatnet2125	Lindås	H	1.96	20	60.6599	5.2592	2125
M52	Storavatnet26964	Sund	H	0.14	24	60.1800	5.0543	26964
M53	Torsteinvatnet	Masfjorden	H	0.03	246	60.7864	5.3337	26192
M54	Steinsvatnet	Gulen	SF	0.39	14	60.8458	5.1127	26088

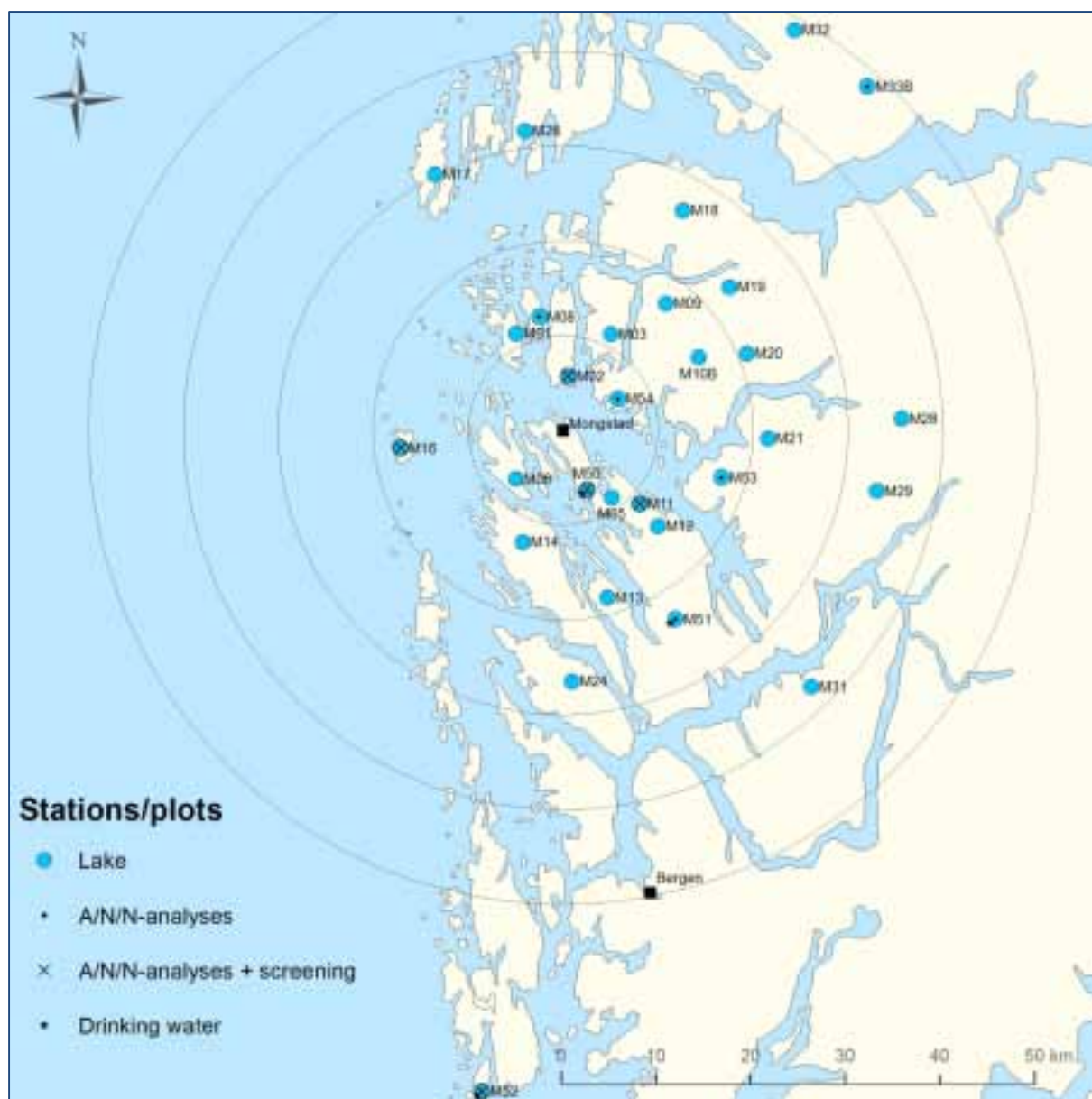


Figure 4.1.3 Map of the Mongstad area showing location of the lakes

## 4.2 Sampling and measurement procedures

### 4.2.1 Ground vegetation: species composition and abundance

At each quadrant six permanent 1 x 1m vegetation quadrants were established along a moisture gradient - two quadrants in dry heath, semi-dry heath, and at wet heath, respectively. The quadrants were divided into 16 0.25 X 0.25m sub-quadrants. All vascular plants, mosses and lichens were recorded in each of 16 sub-quadrants.

#### *Indicator values*

Ellenberg *et al.* (1991) has provided indicator values for vascular plant species that reflects their optimum along several environmental gradients, e.g. light, moisture, pH and nitrogen. The indicator values range from 1-9, with exception of moisture that extends to 12 (10-12 are submerged sites). The scale value 1 refers to the lowest value of each gradient, i.e. less light and low concentrations of nitrogen.

The Ellenberg indicator values were primarily designed for Central Europe, but were modified for the British islands (Hill *et al.* 1999, Hill *et al.* 2007). In this study we use the Ellenberg values modified for UK, as these are expected to better represent general conditions in western Norway.

### **Statistics**

We used the indicator values to obtain environmental approximations for each quadrant according to the vegetation within. This was performed by a weighted average of the indicator values, with weights according to the abundance of present species. The estimated conditions were summarized by classic histograms to visualize the distribution of the observed quadrant. Further, the correlations of estimated conditions to the dominant trends in vegetation were displayed by an ordination by Correspondence Analysis (Oksanen *et al.* 2011). In addition, a correlation matrix was produced to show the linear association between different variables, geographical locations and plant diversity.



**Figure 4.2.1** Vegetation quadrants. (Photo: NFLI, 2011)

### **4.2.2 Trees: growth, vitality and algal biofilm**

Forest sites were established for measuring current height and stem diameter at breast height (DBH) of all pine trees > 5 cm DBH on sites of 400 m<sup>2</sup>, and increment cores were taken from 4 trees per site to compare historical stem growth with the growth after onset of CO<sub>2</sub> capture at Mongstad. A total of eight sites were distributed in the southern (forested) part of the study area to cover the gradient in emissions from Mongstad. In addition, the last two year classes of pine foliage were collected from 5 trees just outside the forest sites to assess the N-status before onset of CO<sub>2</sub> capture. The well-drained pine forest vegetation in Lindås belongs mainly to oceanic mesotrophic blueberry-types (Øvstedal 1985).

Leaf area index (LAI) and crown condition were assessed at these sites. The LAI<sub>e</sub> was measured by quantification of the intensity of diffuse radiation within the forest site and parallel measurements in a nearby open field. The within-forest light intensity relative to the open-field light intensity represents the density of the tree crowns: the darker inside the forest, the denser and presumably healthier are the trees. The relative light intensity was recalculated to effective leaf area index following the Beer-Lambert law:  $LAI_e = c \cdot \log(I_o/I_i)$ , where LAI<sub>e</sub> is effective leaf area index, c is a constant, I<sub>o</sub> is the light intensity in open field, and I<sub>i</sub> is the light intensity inside the forest. At each site LAI was measured at five fixed points, and each measurement was repeated three times. The values presented are the averages of these measurements. The range of LAI is from 1 (open) to 10 (total

darkness). This objective measurement was supplemented by visual crown assessments with binoculars in the field. The assessments included crown density, crown colour and the number of needle year sets.

Autotrophic biofilms of green algae on tree bark are widespread in areas with considerable air pollution levels (ozone, various N compounds) (Bråkenhielm and Quinghong 1995; Freystein et al 2008). Green algae cover is used as a bioindicator for monitoring N concentrations in the air. We assessed the abundance of such green algae coverage on selected birch trees in the vicinity of the forest sites by measuring the horizontal distribution of the algae cover at four different heights (135, 150, 165 and 180 cm). This was done by means of a measuring tape, and presence/absence of algae was recorded at each cm mark. In total 30 geo-referenced birch trees located in proximity of the sites were included in this study.



**Figure 4.2.2** Measurement of biofilms. (Photo: NFLI, 2011)

#### **4.2.3 Soil: samples for chemical analysis**

Soil sampling was limited to the organic layer which is the major active N-pool of the soil. Collection took place adjacent to the 14 sites for the ground vegetation analyses. Soil samples were extracted with a cylinder which can be opened to release the samples without disturbing the soil horizons. Due to the large natural spatial variation in soil chemical composition, soil samples were collected in a geo-referenced 10 x 10 m grid with 25 subsamples, in accordance with the standard method of the Norwegian Forest Inventory (Hämmann and Desaulles 2003).

Each subsample was split into two horizons (L/F and H) after which the different horizons were pooled across subsamples and transferred to plastic bags. In this way there were two samples representing each site, making a total of 28 soil samples from the whole study area. In the field, sampled material was covered with aluminium foil to avoid photo-induced decomposition of critical compounds (e.g. nitrosamines). At the end of the day the soil samples were homogenised manually and split in the lab for subsequent analysis of nitramines/nitrosamines (L/F horizon, n=8), standard chemical analysis (total elements using ICP\_AES, total C and N, NO<sub>3</sub> and NH<sub>4</sub>, L/F and H horizons, n=28), storage (L/F horizon, n=8) and for screening (L/F horizon, n=3). Samples were frozen and stored at -20°C pending chemical analysis.





**Figure 4.2.3** Soil sampling. (Photo: NFLI, 2011)

#### 4.2.4 Plants: samples for chemical analysis

Sampling of plants for chemical analysis was done at the 14 sites and included both cryptogams (lichens and mosses) and a vascular plant. We used the following plant species:

- Moss: *Hylocomium splendens*, which is widely used in ecological state assessments (e.g. Aamlid et al 2000; Solga and Frahm 2006) as it effectively accumulates N and heavy metals. Whole shoots were used to get enough material, not limited to specific age classes.
- Lichen: *Cladonia spp.* was collected as the genus is sensitive to applied N (Britton and Fisher 2010). The initial idea of collecting only *C. portentosa* had to be modified due to modest occurrence.
- Vascular plant: *Calluna vulgaris* is a character species of the heather moorlands and was collected as it rapidly increases the growth and the foliar content of N in response to N input (Edmondson et al. 2010). The last-years shoots were collected for analysis (cf. Power and Collins 2010).

In addition, the last two needle years of pine (2009 and 2010) were sampled during April 2011 from the upper half and southern aspect of five trees in the vicinity of each the 8 forest sites. The needle years were split with a garden scissors. The material was pooled across trees, but with the age groups kept separate.

The plant material was collected directly in paper bags, and plastic gloves were used during collection to avoid contamination. After collection the samples for conventional analysis were dried and subjected to chemical analysis according to Ogner et al. (2000), whereas the moss samples (n=8) intended for analysis of nitramines/nitrosamines and storage (n=8) were stored in a freezer at -20°C pending chemical analysis.



**Figure 4.2.4** Sampling of moss. (Photo: NFLI, 2011)

#### **4.2.5 Benthic algae**

Benthic algae were surveyed according to the established method in Norway (EN 15708:2009) along an approximately 10-m length of river bottom using an aquascope. At each site, visible benthic algae were collected and stored separately in vials. Microscopic algae were collected from ten stones, with diameters ranging between 10 and 20 cm, taken from each site. An area of about 8 x 8 cm from the upper side of each stone was brushed with a toothbrush to transfer the algae into a beaker containing approximately 1 l of river water and a subsample was taken. All samples were preserved with a few drops of formaldehyde. The preserved benthic algae samples were later examined under a microscope, and identified to species level, if possible. Presence of all benthic algae was noted. Diatoms were not included, as their exact determination requires specific preparation procedures. In Norway not enough data on diatom species composition from river sites exist to provide a sufficient basis for comparisons.

The PIT index was calculated for each station according to Schneider and Lindstrøm (2011). PIT is based on indicator values for 153 taxa of benthic algae (diatoms excluded). It ranges from 1.87 to 68.91, and low values indicate low phosphorus concentrations (oligotrophic rivers), while high values indicate high phosphorus concentrations (eutrophic rivers). To calculate a reliable PIT, at least 2 indicator taxa need to be present at a sampling site.

The AIP index was calculated according to Schneider & Lindstrøm (2009). AIP is based in indicator values for 108 taxa of benthic algae. The AIP index ranges from 5.13 to 7.50, and low values indicate acid conditions, while high values indicate neutral to alkali conditions. To calculate a reliable AIP index, at least 3 indicator taxa need to be present at a sampling site.



**Figure 4.2.5** Site 3 LSA RAM (outlet Randals- and Midtbøvatnet, north of Mongstad), sampling and filamentous green algae at LSA RAM (sampling site 3). (Photo: NIVA, 2011)

#### 4.2.6 Lake water: samples for chemical analysis

A total of 30 lakes were sampled on September 20-21, 2011. A helicopter was used for transportation. The helicopter landed close to the sampling site, and the engine was turned off. Samples were collected from about 0.5-1 meter below the surface in an area of the lake that is far away from tributary streams. The water was sampled in a steel container and transferred to clean dark glass bottles. The steel container was rinsed with acetone between each sampling site. An additional 1-L sample was collected for analysis of major components.

The water samples for analysis of amines, nitrosamines, and nitramines (A/N/N) were kept at a low temperature (4-10 °C) until extraction by solid phase extraction (SPE). Nitrosodiethylamine-d6 and N-Nitrosodi-*n*-propylamine-d14 were added to the samples as internal standards. The samples were extracted by a combination of an HLB™ SPE column and an active charcoal SPE column to ensure that all the compounds were taken up by the SPE-columns. A volume of 2.5 L for each sample was preferred for the extraction, but for some samples this was not feasible. The extraction volume for each sample is given in Appendix 10.5. The extraction time was 6-24 h. One blank sample (ion exchanged water) with the sample internal standards was also extracted. After extraction, the SPE cartridges were kept at -20 °C pending chemical analysis.



**Figure 4.2.6** Lake water sampling. (Photo: NIVA, 2011)



## 4.3 Chemical analysis procedures

### 4.3.1 Eutrophication- and acidification-related compounds

Compounds that characterise the important features of the matrices (plant, soil, water) were selected.

#### *Soil*

Soil N enrichment due to N deposition was detected by measuring the following compounds in each layer: C, N, P, S, extractable  $\text{NH}_4$ , water soluble  $\text{NH}_4$  and water soluble  $\text{NO}_3$ .

**Table 4.3.1** Analytical methods and limits of detection (LOD) for soil samples analysed at NFLI (Ogner et al. 2000).

Code	Variable name	Unit	Analytical method	LOD
$\text{NH}_4/\text{NO}_3$	Extractable (1M KCl)	$\text{mg kg}^{-1}$	spectrophotometry, segmented flow	Dependent on dry matter
	Water soluble $\text{NH}_4/\text{NO}_3$	$\text{mg kg}^{-1}$	spectrophotometry, segmented flow	Dependent on dry matter
N	Nitrogen	%	Combustion analysis	0.01
C	Carbon	%	Combustion analysis	0.05
Ca	Calcium	$\text{mg kg}^{-1}$	ICP-OES	18
K	Potassium	$\text{mg kg}^{-1}$	ICP-OES	33
S	Sulphur	$\text{mg kg}^{-1}$	ICP-OES	0.4
Mg	Magnesium	$\text{mg kg}^{-1}$	ICP-OES	1
Na	Sodium	$\text{mg kg}^{-1}$	ICP-OES	90
P	Phosphorus	$\text{mg kg}^{-1}$	ICP-OES	1.1

#### *Plants*

Foliar samples of ground vegetation (moss, lichen, heather, pine) were analysed for total C, N, P, S as well as base cations (Ca, K, Na, Mg).

**Table 4.3.2** Analytical methods and limits of detection (LOD) for plant tissue samples analysed at NFLI (Ogner et al. 2000).

Code	Variable name	Unit	Analytical method	LOD
N	Nitrogen	%	Combustion analysis	0.01
C	Carbon	%	Combustion analysis	0.05
Ca	Calcium	%	ICP-OES	0.002
K	Potassium	%	ICP-OES	0.003
S	Sulphur	%	ICP-OES	0.001
Mg	Magnesium	%	ICP-OES	0.0001
Na	Sodium	$\mu\text{g/g}$	ICP-OES	11.1
P	Phosphorus	%	ICP-OES	0.001

The analysis of eutrophication parameters in plants and soil was performed by NFLI. The analyses were conducted by means of an Elementar Vario EL with TCD detector.  $\text{NH}_4/\text{NO}_3$  was analysed by a Skalar San+ segmented flow analysis (SFA) (see Ogner et al. 2000).

#### *Surface water*

Parameters relevant for assessing the nutrient status (total N, nitrate, ammonium, total phosphorus) of the lakes were included in the analytical programme.

Ionic strength and pH affect several processes in natural aqueous systems and are essential for chemical characterisation of natural waters. All major ions and total organic carbon (TOC) were determined. This provides the basis for assessment of acidification, and the results can be compared with those from the surveys of 1988-1991 (Traaen and Henriksen, 1988-1992).

**Table 4.3.3** Analytical methods and limits of detection (LOD) for surface water chemical parameters.

<i>Code</i>	<i>Analyte</i>	<i>Analytical method</i>	<i>LOD</i>	<i>Unit</i>
pH	pH	Potentiometry	-	
Kond	Conductivity	Electrometry	0.05	mS m <sup>-1</sup> 25°C
Ca	Calcium	Ion chromatography	0.02	mg L <sup>-1</sup>
Mg	Magnesium	"	0.02	mg L <sup>-1</sup>
Na	Sodium	"	0.02	mg L <sup>-1</sup>
K	Potassium	"	0.02	mg L <sup>-1</sup>
Cl	Chloride	"	0.03	mg L <sup>-1</sup>
SO <sub>4</sub>	Sulphate	"	0.04	mg L <sup>-1</sup>
NO <sub>3</sub> -N	Nitrate	"	1	µg N L <sup>-1</sup>
Alk	Alkalinity	Potentiometric titration to pH = 4.5	0.01	mmol L <sup>-1</sup>
TOC	Total organic carbon	Oxidation to CO <sub>2</sub> with UV/persulphate (IR-detection)	0.10	mg C L <sup>-1</sup>
Tot-N	Total Nitrogen	Automated photometry	10	µg N L <sup>-1</sup>
NH <sub>4</sub> <sup>+</sup>	Ammonium	Ion chromatography	5	µg N L <sup>-1</sup>
Tot-P	Total phosphorus	Automated photometry	1	µg P L <sup>-1</sup>
Al/R	Reactive aluminium	Automated photometry	10	µg Al L <sup>-1</sup>
Al/II	Non-labile aluminium	Automated photometry	10	µg Al L <sup>-1</sup>

Labile inorganic aluminium (LAI) was defined as the difference between reactive Al and non-labile Al. The samples were analysed at NIVA.

#### 4.3.2 Amines, nitrosamines and nitramines

Ten water samples, eight soil samples and eight plant samples were analysed for several amines, nitrosamines and nitramines.

##### *Amines*

The amine analyses were conducted at NILU using an in-house validated method based on derivatization to improve the analyte behaviour towards reversed phase chromatography. Aliquots of the water samples were prepared by adding a buffer solution and the derivatizing agent. After a defined reaction time a sample aliquot was further worked up by solid phase extraction in order to reach the lowest detection limits. The instrumental analyses were performed on a Waters UPLC liquid chromatography system equipped with an auto-sampler and a Waters LCT Premier XE mass spectrometer. The solid samples (biota and soil) were homogenized and extracted with acetonitrile, methanol, water and ultra-sonic agitation. The extracts were cleaned-up by solid phase extraction and then treated by the same procedure as for water samples prior to the chemical analyses.

The analytical method performance was validated by spiking experiments and control samples of the seven target amines in tap water, soil and moss. All analysis results were blank level corrected by subtracting the average blank value plus one standard deviation obtained by analyses of 10 parallel MQ-water samples. The method performance is summarized in **Table 4.3.4**.

**Table 4.3.4** Amines analysed for and analytical limit of detection for individual components.

<i>Amine</i>		<i>CAS number</i>	<i>M.W. g mol<sup>-1</sup></i>	<i>LOD ng g<sup>-1</sup> biota/soil</i>	<i>LOD ng L<sup>-1</sup> water</i>
Methylamine (MA)	CH <sub>3</sub> NH	74-89-5	31	1	10
Ethylamine (EA)	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	75-04-7	45	1	10
Dimethylamine (DMA)	(CH <sub>3</sub> ) <sub>2</sub> NH	124-40-3	45	1	10
Diethylamine (DEA)	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NH	109-89-7	73	1	10
Ethanolamine (MEA)	(CH <sub>2</sub> ) <sub>2</sub> OHNH <sub>2</sub>	141-43-5	61	1	10
2-amino-2-methyl-propanol (AMP)	C <sub>4</sub> H <sub>11</sub> NO	124-68-5	89	1	10
Piperazine (PIP)	(CH <sub>2</sub> ) <sub>4</sub> (NH) <sub>2</sub>	110-85-0	86	1	10

*Nitramines and nitrosamines*

The nitrosamines and nitramines were analysed at NILU by in-house validated methods based on own experience and the principles found in US EPA method 521. The samples were spiked with labelled and unlabelled nitrosamines as internal standards. After work up on solid phase extraction cartridges one aliquot of the sample was analysed by liquid chromatography (UPLC and HPLC) combined with high resolution mass spectrometry and one sample aliquot was analysed by gas chromatography (GC) combined with the Thermal Energy Analyser (TEA) (Cambridge Scientific Instruments). The solid samples (biota and soil) were homogenized and extracted with acetonitrile, methanol and ultra-sonic agitation, and the extracts were cleaned-up with solid phase extraction prior to analysis by UPLC and HPLC combined with MS and GC/TEA.

The analytical method performance was validated by spiking experiments and control samples of the target nitrosamines and nitramines in tap water, soil and moss. In addition, known amounts of nitrosamines and nitramines were added to selected authentic sample extracts in order to conduct a matrix match calibration. The method performance is summarized in **Table 4.3.5** and **Table 4.3.6**.

**Table 4.3.5** List of nitramine compounds for testing.

<i>Nitramine</i>	<i>LOD ng g<sup>-1</sup> biota/soil</i>	<i>LOD ng L<sup>-1</sup> water</i>
N-Nitro-methylamine	2	1.5
N-Nitro-dimethylamine	2	1
N-Nitro-ethanolamine	2	0.8
2-methyl-2-nitroamino-propanol	2	0.7
N-Nitro-piperazine	2	0.9

The limits of detection for all compounds were estimated (S/N=3) from analysis of a quantification standard and corrected for the sample analyte recovery.

**Table 4.3.6** List of nitrosamines analysed.

<i>Nitrosamines</i>	<i>LOD ng g<sup>-1</sup> biota/soil</i>	<i>LOD ng L<sup>-1</sup> water</i>
Nitrosodimethylamine (NDMA)	1	0.7
Nitrosodiethylamine (NDEA)	1	0.7
N-nitrosodiethanolamine (NDELA)	1	1.1
Nitroso-N-methylethylamine	1	0.7
Nitroso-N-propylamine	1	0.7
Nitrosomorpholine	1	0.7
Nitrosopyrrolidine	1	0.7
Nitrosopiperazine	1	0.7
Nitrosopiperidine	1	0.7

**Table 4.3.7** Analytical method performance for measurement of amines, nitrosamines and nitramines

<i>Compound class</i>	<i>Precision water (% RSD)</i>	<i>Precision Biota and soil (% RSD)</i>	<i>Recovery Water (%)</i>	<i>Recovery Soil and Biota (%)</i>	<i>Estimated biota and soil LOD (ng/g)****</i>	<i>Estimated water LOD (ng/L)</i>
Amines	<10	<25	>95	>75	1	10*
Nitrosamines	<15	<30	60-100	>50	1	0.7-1.1**
Nitramines	<15	<30	30-95	>40	2	0.8-1.5***

\*: 10 mL water sample

\*\* : 1500 mL water sample extracted as 3 x 500 mL

\*\*\*: 1000 mL water sample extracted as 3 x 333 mL

\*\*\*\*: 2 g sample

### 4.3.3 Analytical screening

The amine that will be first tested at TCM for CO<sub>2</sub> capture will be 2-aminoethanol (MEA), and the degradation process of this compound has been studied in detail (Nielsen et al., 2010). However, in the future other amines may be considered for use, possibly resulting in other amine, nitrosamine and nitramine compounds entering the environment. It was therefore important to perform an analytical screening of a sub-set of samples to detect the presence of functional groups from amine, nitrosamines and nitramine compounds.

NIVA carried out the screening for these unspecified compounds. The instruments used include a GC-TOF-MS and a LC-MS-MS which can be used to identify a broad range of organic compounds. Sample extracts were run to detect both polar (LC-MS-MS) and non-polar (GC-TOF-MS) compounds. Identification of the compounds was done using accurate mass determination. All of the methodologies and raw data were saved and backed up so that methods can be repeated, enabling results to be compared in order to identify changes in contaminant composition in subsequent years. Analysis was qualitative but where possible semi-quantitative data were collated.

Only samples from stations suspected to receive the highest emissions were subjected to analytical screening. Consequently, 5 water samples, 3 plant and 3 soil samples were analysed. The extraction of samples proceeded as described for storage of water samples. In addition to the samples, a blank sample (ion exchanged water with internal standards added) was extracted for reference purposes.

#### *Sample extraction*

Soil (10 g) and moss (2-5 g) samples were weighed out and 100 ng NDMA-d<sub>6</sub> added to each sample to act as an internal standard. Samples were double shaker extracted, initially for 2 hours with

methanol (2% ammonium hydroxide) followed by 2 hours with dichloromethane (DCM). The solvent extracts were combined and the DCM removed by evaporation under nitrogen.

The methanol extract was diluted 10x into ultrapure water in preparation for clean-up by solid phase extraction (SPE) using the same method used the extraction of water samples. Oasis HLB™ (Waters, Sweden) and activated carbon (EPA method 521, Sigma-Aldrich) were connected in series. The cartridges were conditioned with the addition of methanol followed by water before the samples extracted under vacuum.

The analytes were eluted from the activated carbon cartridges with DCM. The eluent was evaporated to approximately 1 mL under nitrogen and the extract split in half for LC/MS and GC/MS analysis. The LC/MS extract was solvent exchanged to methanol and water and the GC/MS extract concentrated further before GC/MS analysis.

#### *Instrumental analysis*

##### Gas chromatography/time-of-flight/mass spectrometry (GC-ToF-MS)

Samples were analysed by GC-ToF-MS (GCT Premier, Waters, Sweden) with and without derivatisation. Samples were derivatised with the addition of BSTFA + TMCS in iso-octane. The GC-ToF-MS was operated with greater than 8000 resolution, with a source temperature of 180 °C and an injector temperature of 270 °C. The initial oven temperature was 100 °C with a 2 minute hold time; the temperature was then ramped at 10 °C/min to 180 °C and held for 10 minutes. The MS scan range was 50-800 m/z. The column used was a DB-5 MS column (30 m x 0.25 mm i.d. x 0.25 µm film thickness).

The data obtained is stored and available for reprocessing at a later date (if necessary).

##### Ultra performance liquid chromatography/tandem mass spectrometry (LC/MS/MS)

Samples were analysed by LC-MS-MS (UPLC-Quattro Premier XE, Waters, Sweden). The extracts were analysed with and without derivatisation. The solvent extracts were evaporated under nitrogen and derivatized by the addition of 100 µL pyridine and 50 µL acetic anhydride. The derivatization was allowed to occur over 2 hours at 40 °C. The derivatization reagents were evaporated under nitrogen, and samples were reconstituted in mobile phase for LCMS analysis.

Analytes were separated using a gradient elution program with water (ammonium acetate) and methanol (ammonium acetate). The analytical details are as follows:

Column: Acquity UPLC BEH C18, 2.1 x 50mm, 1.7µm. Temp: 50 °C

Mobile Phase A: 0.1 % formic acid

Mobile Phase B: 0.1 % formic acid in methanol

Flow rate: 0.6 mL/min

Gradient Profile: Linear 7 minute gradient from 100 % A to 100 % B.

#### MS

Scanning data acquisition carried out in both positive and negative mode.

Electrospray positive mode, 20v Cone. Full-scan MS acquisition from m/z=50 to m/z=500

Electrospray negative mode, 20v Cone. Full-scan MS acquisition from m/z=50 to m/z=500

The data obtained is stored and available for reprocessing at a later date (if necessary).

#### **4.3.4 Storage of samples**

Samples from all locations were collected for the purpose of storage at -20 °C for a period of 5 years. The plants and soil were sampled in August and kept frozen (-20 °C) until shipment to Oslo. In Oslo,

the material was also kept frozen (-20 °C) until shipment to the storage freezer. The water samples were kept at a low temperature (4-10 °C) until extraction by solid phase extraction (SPE). The samples were added Nitrosodiethylamine-d6 and N-Nitrosodi-*n*-propylamine-d14 as internal standards. The samples were extracted by a combination of an HLB™ SPE column and an active charcoal SPE column to ensure that all the compounds were taken up by the SPE-columns. We tried to extract 2.5 L for each sample, but for some samples this was not feasible. The sample volume for each sample is given in Appendix 10.5. The extraction time was 6-24 h. One blank sample (ion exchanged water) with the sample internal standards was also extracted. After extraction, the SPE cartridges were kept at -20 °C. The samples were transported to the external freezer storage (Frigoscandia at Furuset). The samples are placed in NIVA Pall number 23, box 11, and are marked in NIVAs freezing database with code 13996 (O-11183).



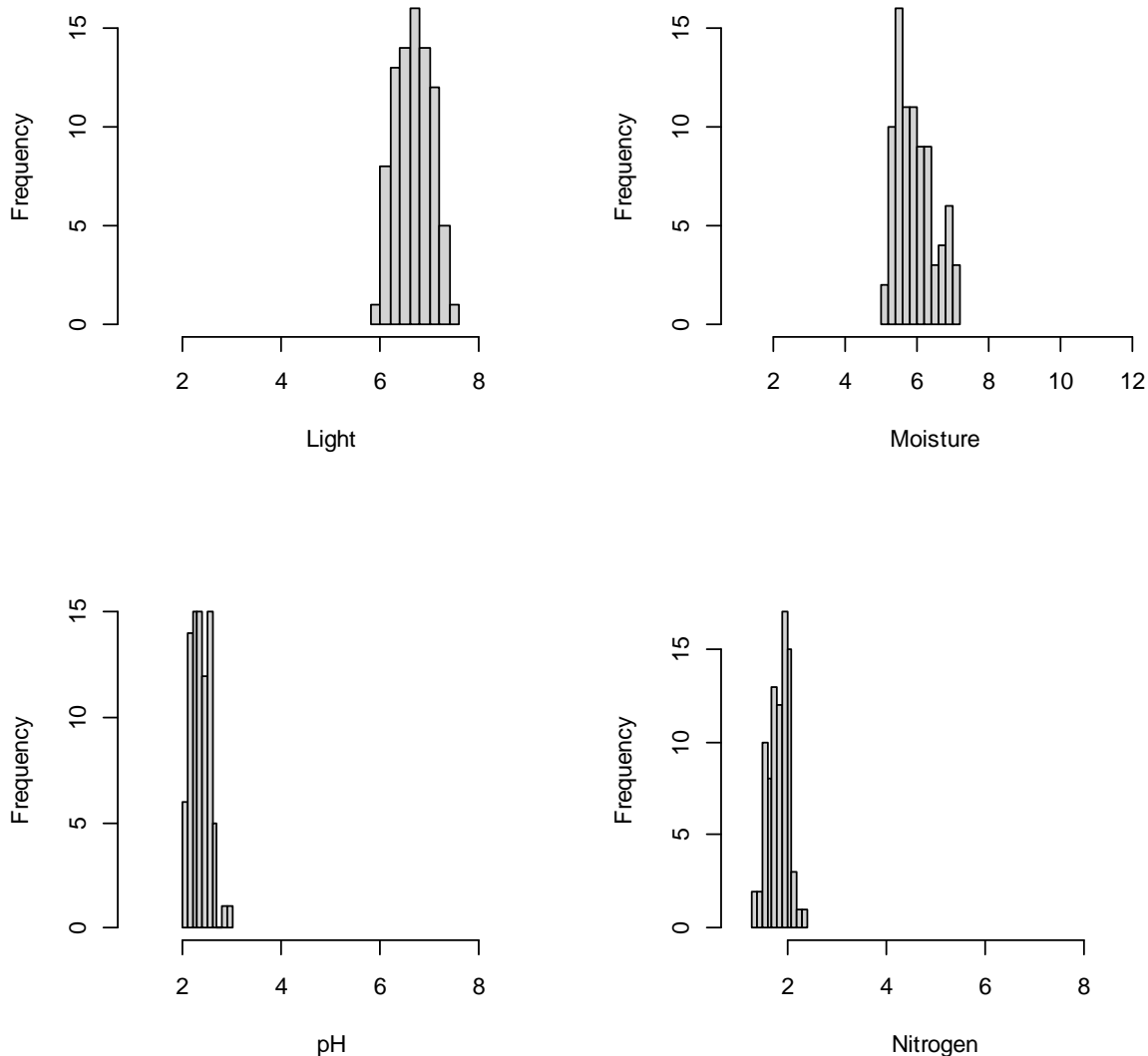
**Figure 4.3.1** Extraction of water samples for storage. (Photo: NIVA, 2011)

## 5. Results

### 5.1 Terrestrial ecosystem measurements

#### 5.1.1 Ground vegetation

The selected sites represent heathland species with their optimum in areas with low pH and low nitrogen concentration (**Figure 5.1.1 c and d**). Deposition of nitrogen have a strong potential to influence species composition in the selected quadrants as these today are recognized as generally infertile sites (Ellenberg nitrogen value <3). The sampled vegetation was found to indicate places in the range from well-lit to partially shaded environments (Fig. 1a), which is typical of the vegetation in the open heathlands. The quadrants are also found to have moderate soil moisture, which corresponds to the design of the sites, with 2 quadrants each in dry, moderate and wet terrain, respectively.



**Figure 5.1.1** Histogram of the quadrant-specific Ellenberg values estimated for each quadrant based on the abundance of the species present. N=84 (14 sites, 6 quadrants per site).

The species richness of vascular plants was positively correlated to pH, moisture and nitrogen (Appendix 10.6). The species richness of mosses showed a similar trend, additionally to a slight negative influence of light. The lichens were found to avoid moist conditions, and were often associated with drier ridges, i.e. the uppermost quadrants of the local transects. In addition, there was a low correlation between the geographical positions and other parameters.

As anticipated by the predefined sampling design all sites were of the *Calluna vulgaris* heathland type, but some differences in the vegetation were detected (Appendix 10.7). The dominant variables following separating different quadrants are nitrogen, light, moisture and pH. This suggests that the vegetation, although nutrient poor, is differentiated by nutrient availability. Further, at present the geographic distribution of the quadrants that are associated with slightly richer conditions (left hand side in Appendix 10.7) are not in the vicinity of TCM.

## 5.1.2 Trees

### Forest growth

The forest sites were rather heterogeneous with respect to the stand characteristics (Table 5.1.1), reflecting different ages, histories and growing conditions. The standing volume of pine displayed a decrease from north to south, and F8 contained only 15% of the volume of F1. Accordingly, height and DBH varied in a similar manner, although not so pronounced.

**Table 5.1.1** Forest site characteristics. Height, DBH (diameter at breast height), crown density and LAI (Leaf Area Index, 1 (open)-10 (dark)) are average values for trees at each site. Trees refer to sizes > 5 cm DBH

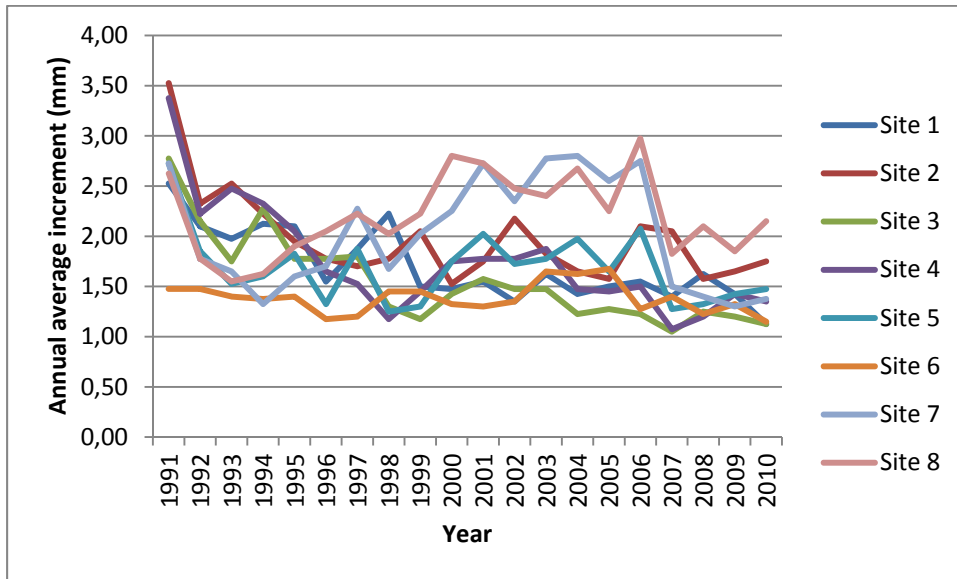
Site	Standing volume (m <sup>3</sup> /ha)	No of trees/ha	Height (m)	DBH (cm)	Crown density (%)	LAI
F1	463	1650	17.5	20.7	92.5	2.14
F2	360	1175	16.6	22.0	85.8	2.00
F3	351	1225	18.0	20.6	84.8	1.90
F4	344	1275	16.4	20.9	82.8	2.14
F5	134	1125	13.7	14.8	86.2	1.72
F6	174	1375	13.8	15.5	86.5	1.77
F7	162	1775	12.6	13.4	88.5	2.43
F8	68	1150	11.3	11.4	87.5	1.56

The crown density on the surveyed forest sites was medium to high, ranging from 83 to 93%, and with an average of 87%. However, the condition of the trees was variable. Actually, 39% (F8) to 71% (F7) of the trees had one or more injuries, either due to climatic stress from wind and snow, to fungi/insects or related to heavy competition from neighbouring trees.

LAI (Leaf Area Index) is a measure of the light transmission through the forest canopy. LAI-values in the range 1.56-2.43 reflect presence of rather open pine forests with abundant light reaching the forest floor. There was no spatial pattern in LAI and number of trees/ha along the transect, but light transmission through the individual sites was strongly dependent on density of trees. Thus, number of trees/ha and LAI were significantly correlated ( $r=0.78$ ).

Radial growth at breast height over the last two decades (Figure 5.1.2), as measured by increment cores, has been consistently high at sites F2, F7 and F8, and conversely, low at sites F3 and F6. Thus, when averaged over the last 10 years diameter growth was negatively correlated to present standing volume and DBH ( $r \leq -0.68$ ). This reflects the decreasing radial growth response as the stand develops and competition for light and nutrients increases. As shown in Table 5.1.2 correlation for growth was higher between adjacent sites than between sites more distant.





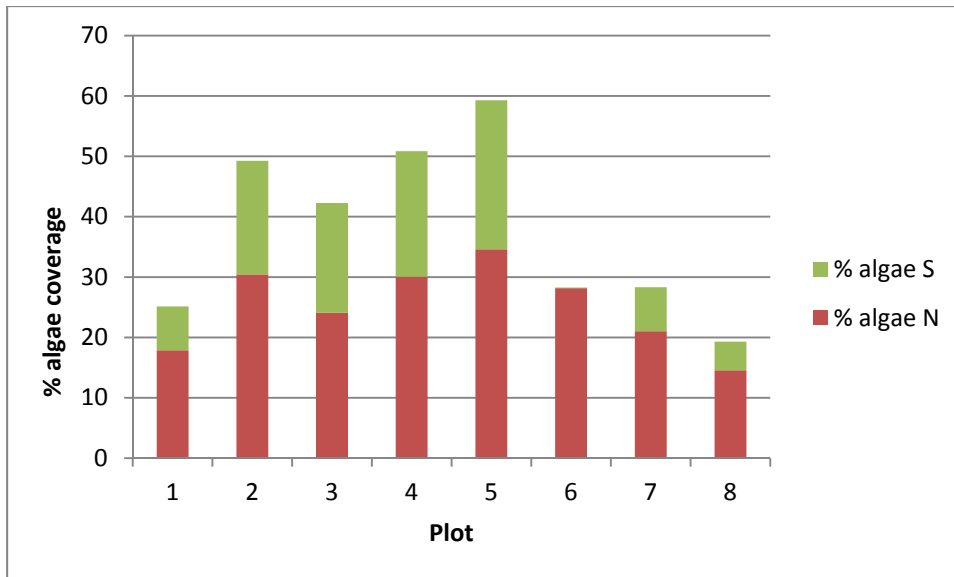
**Figure 5.1.2** Radial growth. Annual increment at each site (means of five trees) during the last 20 years.

**Table 5.1.2** Correlation matrix for annual ring widths (1991-2010). Bold values are significant at the  $p < 0.01$  level.

Plot	F1	F2	F3	F4	F5	F6	F7	F8
F1	1.00	<b>0.63</b>	<b>0.80</b>	<b>0.69</b>	0.39	0.20	-0.04	-0.28
F2	<b>0.63</b>	1.00	<b>0.73</b>	<b>0.83</b>	<b>0.56</b>	0.15	0.13	-0.06
F3	<b>0.80</b>	<b>0.73</b>	1.00	<b>0.90</b>	<b>0.60</b>	0.04	0.08	-0.15
F4	<b>0.69</b>	<b>0.83</b>	<b>0.90</b>	1.00	<b>0.68</b>	0.20	0.20	-0.04
F5	0.39	<b>0.56</b>	<b>0.60</b>	<b>0.68</b>	1.00	0.21	<b>0.70</b>	<b>0.57</b>
F6	0.20	0.15	0.04	0.20	0.20	1.00	0.44	0.05
F7	-0.04	0.13	0.08	0.20	<b>0.70</b>	0.44	1.00	<b>0.83</b>
F8	-0.28	-0.06	-0.15	-0.04	<b>0.57</b>	0.05	<b>0.83</b>	1.00

**Algae coverage**

The cover of algae on birch stems was extensive and showed large variation (20 to 60% of the circumference), but no geographical trend. The cover on the northern aspects of the stems was consistently larger than on the southern aspects.

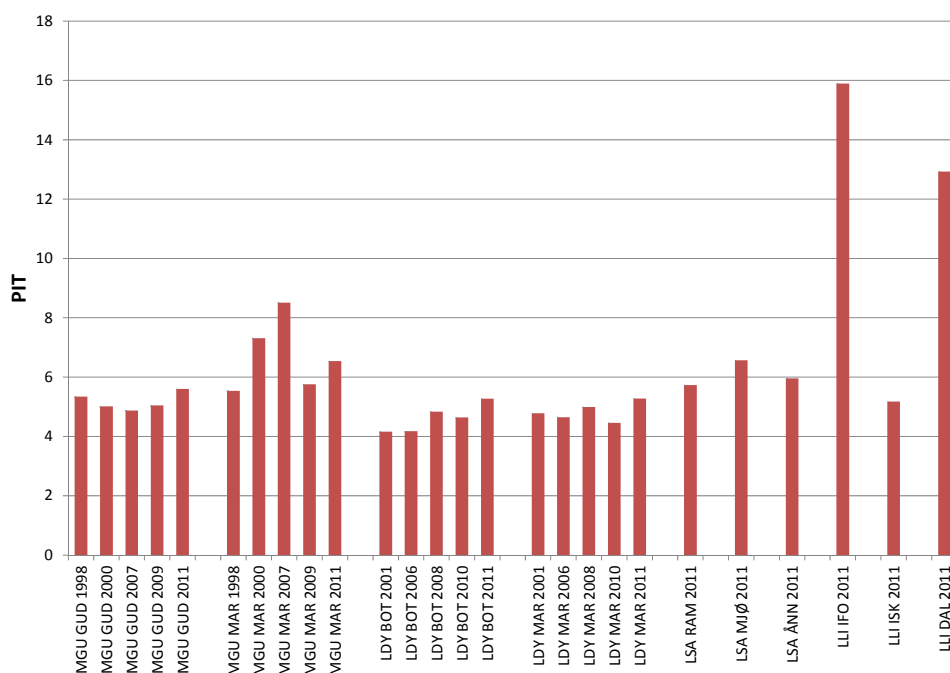


**Figure 5.1.3** Coverage of algae on southern and northern aspect of birch stems. Means of cover at four heights in five trees on each site.

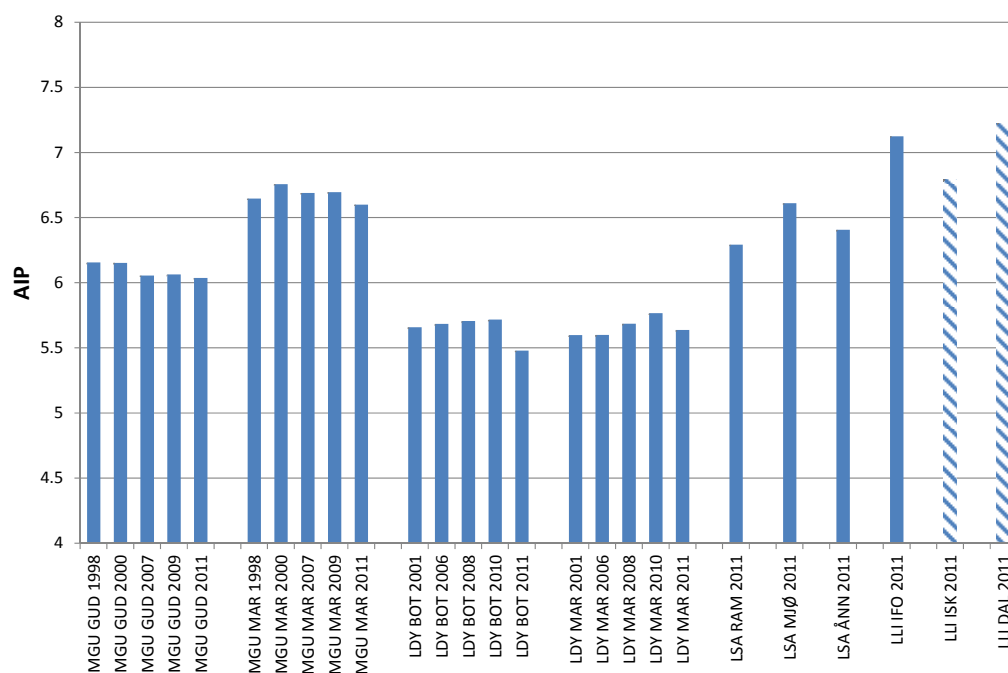
## 5.2 Aquatic ecosystem measurements

### 5.2.1 Benthic algae

NIVA has data for previous years on benthic algae species composition and abundance from the two sites in the Flekke-Guddal and the two sites in the Yndesdal catchments (Directorate for Nature Protection 2010, Directorate for Nature Protection 2011). The PIT index shows that all these four sites are oligotrophic. The two sites in the Yndesdal catchment (LDY BOT and LDY MAR) generally had the lowest PIT values. PIT indices at all three sites north of Mongstad (LSA RAM, LSA MJØ, LSA ÅNN) were in the same range as in Yndesdal and Flekke-Guddal, such that these sites are comparable to each other. LLI ISK is the only site south of Mongstad which also had a low PIT index. The two other sites (LLI IFO and LLI DAL) are meso- eutrophic (i.e. have a higher PIT index due to enhanced concentrations of plant nutrients). The source of these nutrients is probably agricultural activity.



**Figure 5.2.1** PIT index (periphyton index of trophic status) at 10 sampling sites. Data for previous years for the sites in the Flekke-Guddal and Yndesdal catchments are from the NIVA databank (Directorate for Nature Protection 2010, Directorate for Nature Protection 2011).



**Figure 5.2.2** AIP index (acidification index periphyton) at 10 sampling sites. Data for previous years for the sites in the Flekke-Guddal and Yndesdal catchments are from the NIVA databank (Directorate for Nature Protection 2010, Directorate for Nature Protection 2011). Due to the occurrence of fewer than 3 indicator taxa, the AIP index at LLI ISK and LLI DAL is indicative only.

The Yndesdal catchment is more acidic than the Flekke-Guddal catchment, and this is reflected in the AIP index (lowest values at LDY BOT and LDY MAR). The AIP index at the three sites north of Mongstad (LSA RAM, MJØ and ÅNN) indicates slightly acidic conditions and is in the same range as in

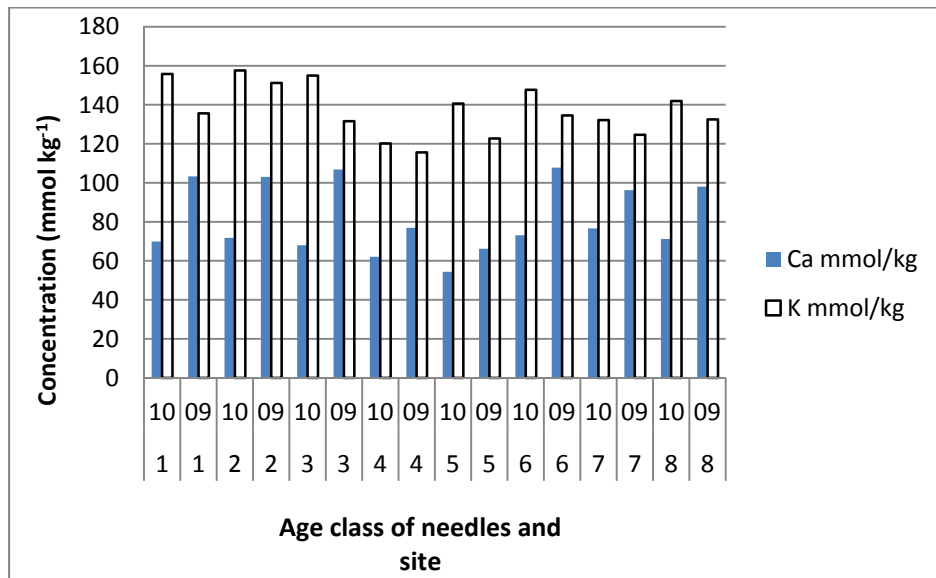
the Flekke-Guddal catchment. In contrast, the sites south of Mongstad are not acidic. At two of the sites, less than three indicator taxa were found, such that the AIP index is indicative only. The higher AIP index south of Mongstad likely is related to slightly different mineralogy of soil and overburden in the catchments compared to the other sampling sites.

All the species and their abundances are listed in Appendix 10.4.

### 5.3 Chemical analyses

#### 5.3.1 Eutrophication and acidification parameters

Pine needles: The nutrient elements N, K, P and Mg were found at higher concentrations in the 2010 age class than the 2009 age class. The opposite pattern was found for Ca, Fe and Na where the highest concentrations were present in the 2009 age class (Table 5.3.1, **Figure 5.3.1**). There were generally no geographic patterns in the concentrations of the elements, except for N which showed an overall but slight decrease from north to south. Maps showing the geographical distributions of several elements are presented in Appendix 10.8.



**Figure 5.3.1** Opposing patterns of Ca and K concentrations in current (2010) and last year's needles (2009) in pine at the different forest site.

**Table 5.3.1** Needle chemistry. Concentrations of nutrient elements and Na in needle age groups from 2010 and 2009 (means of five trees/site) at the forest site, ranked in order of increasing distance from Mongstad (southwards). Limit of detection given in parentheses.

<i>Site</i>	<i>Age group</i>	<i>Ca</i> <i>mmol</i> <i>kg<sup>-1</sup></i> <i>(0,4)</i>	<i>Fe</i> <i>mmol</i> <i>kg<sup>-1</sup></i> <i>(0,08)</i>	<i>K</i> <i>mmol</i> <i>kg<sup>-1</sup></i> <i>(0,9)</i>	<i>Mg</i> <i>mmol</i> <i>kg<sup>-1</sup></i> <i>(0,05)</i>	<i>P</i> <i>mmol</i> <i>kg<sup>-1</sup></i> <i>(0,2)</i>	<i>S</i> <i>mmol</i> <i>kg<sup>-1</sup></i> <i>(0,28)</i>	<i>Na</i> <i>mmol</i> <i>kg<sup>-1</sup></i> <i>(0,48)</i>	<i>N</i> <i>%</i>	<i>C</i> <i>%</i>
F1	2010	69.9	1.09	155.8	50.6	52.3	33.35	11.07	1.69	53.34
	2009	103.3	1.26	135.6	42.1	44.9	33.61	24.08	1.69	53.60
F2	2010	71.8	0.67	157.6	51.3	55.4	32.98	10.43	1.80	53.35
	2009	103.0	0.94	151.2	36.5	48.9	33.16	31.50	1.68	53.28
F3	2010	68.0	1.05	155.0	58.0	49.2	32.10	6.81	1.72	53.38
	2009	106.8	1.59	131.6	51.9	46.6	35.00	40.93	1.69	53.84
F4	2010	62.1	0.85	120.2	50.0	36.3	33.43	9.14	1.96	53.55
	2009	76.9	1.15	115.6	45.4	31.9	32.66	31.92	1.93	53.29
F5	2010	54.4	0.80	140.6	45.2	38.9	29.68	6.93	1.34	54.35
	2009	66.2	1.08	122.7	37.8	31.6	26.89	17.00	1.19	53.84
F6	2010	73.1	0.79	147.7	47.6	46.5	31.63	8.57	1.61	52.72
	2009	107.8	1.04	134.5	40.4	42.6	32.59	17.64	1.65	52.81
F7	2010	76.6	0.75	132.2	46.1	52.0	30.93	7.39	1.48	53.44
	2009	96.2	0.88	124.6	34.0	42.7	27.86	17.37	1.30	53.07
F8	2010	71.2	0.67	141.9	38.8	44.2	27.54	5.59	1.42	53.63
	2009	98.0	0.94	132.5	33.7	37.3	27.31	13.89	1.28	52.76

**Table 5.3.2** Concentrations of nutrient elements and Na (detection limits in parenthesis) in different species at the vegetation plots.

Species	Site	Plot	Ca mmol kg <sup>-1</sup> (0.4)	K mmol kg <sup>-1</sup> (0.9)	Mg mmol kg <sup>-1</sup> (0.05)	P mmol kg <sup>-1</sup> (0.2)	S mmol kg <sup>-1</sup> (0.28)	Na mmol kg <sup>-1</sup> (0.48)	N %	C %
<i>Calluna vulgaris</i>	G1	1	78.3	123.5	68.8	29.4	36.98	19.17	1.29	53.73
	G2	2	78.1	141.3	59.7	30.8	39.81	20.06	1.26	54.50
	G3	3	87.1	145.2	62.3	27.2	39.82	21.34	1.38	55.98
	G4	4	93.2	133.6	73.0	29.4	41.36	17.56	1.59	54.74
	G5	5	82.2	147.3	61.0	31.2	39.58	14.37	1.40	54.51
	G6	6	92.9	132.6	76.7	34.4	41.09	20.46	1.31	54.51
	G7	7	84.7	139.7	54.3	23.0	37.09	18.66	1.30	55.20
	G8	8	78.7	131.4	61.9	31.3	37.54	60.54	1.10	55.25
	G9	9	96.2	104.7	63.5	22.5	34.17	28.16	0.99	54.78
	G10	10	100.2	98.1	64.5	17.4	35.16	46.07	1.03	54.97
	G11	11	92.8	132.0	57.6	18.6	32.78	37.81	0.98	54.83
	G12	12	92.0	107.9	57.8	19.6	33.33	17.94	1.05	55.49
	G13	13	101.4	109.6	62.6	16.7	32.76	15.78	1.02	55.55
	G14	14	92.1	102.9	72.8	16.1	31.04	16.06	1.07	54.40
<i>Cladonia spp</i>	G1	1	15.6	25.0	22.5	7.8	13.93	4.05	0.39	46.62
	G2	2	28.1	26.9	29.4	8.8	18.12	3.65	0.55	47.65
	G3	3	12.8	19.0	19.2	6.3	18.86	2.90	0.54	47.09
	G4	4	18.7	30.8	23.4	9.1	19.45	2.72	0.57	46.98
	G5	5	23.3	34.0	26.6	9.5	19.91	3.33	0.62	47.05
	G6	6	16.7	32.8	22.2	11.1	15.79	4.79	0.52	47.15
	G7	7	21.5	26.6	23.9	7.8	20.18	3.65	0.62	47.59
	G8	8	21.5	29.3	33.9	11.1	19.18	15.55	0.46	47.53
	G9	9	19.1	28.2	24.1	8.4	17.15	3.54	0.55	47.22
	G10	10	14.6	24.5	20.3	7.9	13.27	4.43	0.40	46.93
	G11	11	11.5	20.1	22.7	7.0	25.27	13.36	0.59	46.85
	G12	12	18.2	29.3	22.0	8.0	20.43	3.51	0.59	47.33
	G13	13	24.8	24.5	23.0	7.9	24.20	3.73	0.68	47.99
	G14	14	13.1	27.5	20.3	9.4	24.85	3.96	0.59	47.08
<i>Hylocomium splendens</i>	G1	1	88.0	54.0	63.6	24.5	27.73	8.78	0.96	50.68
	G2	2	102.1	69.2	70.9	23.5	30.13	7.37	0.99	50.28
	G3	3	124.4	31.7	61.2	15.6	33.75	8.04	1.07	48.57
	G4	4	91.0	77.3	56.7	23.5	25.05	7.10	0.85	50.51
	G5	5	91.9	62.5	66.8	21.8	32.42	7.49	1.05	50.16
	G6	6	86.3	67.9	69.9	33.8	26.26	6.89	0.95	50.26
	G7	7	82.7	79.6	82.8	32.1	35.39	7.31	1.00	49.42
	G8	8	71.0	72.8	75.4	34.8	25.48	16.92	0.95	49.65
	G9	9	93.6	79.4	70.8	25.5	31.20	7.35	1.04	50.84
	G10	10	100.8	57.5	71.3	18.2	27.26	5.65	0.89	50.42
	G11	11	77.7	90.5	66.6	35.2	21.46	11.02	0.74	49.27
	G12	12	74.9	61.3	61.2	22.6	36.85	7.96	1.21	50.15
	G13	13	136.9	54.0	62.0	18.7	36.00	8.98	1.16	50.96
	G14	14	98.9	64.1	61.3	19.0	26.44	5.56	0.85	50.83

Heather (*Calluna vulgaris*): In *Calluna* the variation pattern in concentrations of N, K, P and S was similar among the sites ( $r \geq 0.72$ ,  $p < 0.01$ ), with generally higher values at Lindås peninsula in the vicinity of Mongstad than in Gulen to the north of Fensfjorden. An opposite trend was observed for Ca, whereas Mg displayed no particular geographic structure (**Table 5.3.2**).

Lichen (*Cladonia spp*): In *Cladonia* a significant correlation was found between the pairs P - K and P - Mg ( $r \geq 0.56$ ,  $p < 0.05$ ), with the highest concentrations at Lindås peninsula and Fedje. Also the concentrations of N and S were correlated ( $r = 0.79$ ), but there was no discernible geographic structure in these elements, nor in Ca (**Table 5.3.2**).

Moss (*Hylocomium splendens*): In *Hylocomium* the variation in concentration of P was significantly correlated to K ( $r = 0.74$ ) and Mg ( $r = 0.57$ ), and there was a tendency of higher concentrations in western sites. Similarly, N and S were strongly correlated ( $r = 0.9$ ), but there was no geographic pattern in the concentrations of these elements (**Table 5.3.2**).

Na is not a nutrient element in plants, but is included here to demonstrate different exposure to salt spray from the sea. Thus, irrespective of species (**Table 5.3.2**), the highest concentration was found at the westernmost site at Fedje (plot 10), but the levels were also elevated at exposed sites in Gulen (e.g. site 13) (**Table 5.3.2**). Mg, Ca, S and K are also major constituents of salinity in sea water (Brown et al. 1995), and it is likely the high concentrations of Mg in *Cladonia* at Fedje is due to sea spray (**Table 5.3.2**).

#### Soil

Data for concentrations in soil are shown in **Table 5.3.3**.

Nitrate concentrations were at or below the detection limit in both KCl and water extracts for both soil horizons at all sites. Ammonium concentrations, on the other hand, were almost all above the detection limit. Most nitrogen in the soil is probably in the form of organic-N, rather than  $\text{NH}_4$  or  $\text{NO}_3$ .

Principal component analysis suggested close links between C, total N, P, S and  $\text{NO}_3$ : this group is likely to be related to soil organic matter. Ca, Mg and Na appeared to be linked, which may be related to sea salt inputs, while  $\text{NH}_4$  was separate from both major groups. K appeared to be related in part to the group containing C, total N, P, S and  $\text{NO}_3$ , and in part to  $\text{NH}_4$ .

Data for concentrations in soil are shown in **Table 5.3.3**

**Table 5.3.3** Concentrations of nutrient elements, Na and C in soil at the vegetation sites. Concentrations in  $\text{mmol kg}^{-1}$  soil unless otherwise specified. UD = under the detection limit. The detection limit was  $0.03\text{-}0.11 \text{ mmol kg}^{-1}$  in KCl extractable and water soluble  $\text{NO}_3\text{-N}$ , and  $0.46\text{-}0.48 \text{ mmol kg}^{-1}$  for water soluble  $\text{NH}_4\text{-N}$ . Differences in detection limit are due to variation in sample sizes prepared for analysis.

Soil horizon	Site	Plot	Ca	K	Mg	Na	P	S	C (%)	N (%)	C/N (g/g)	KCl-extractable			Water-soluble		
												NH <sub>4</sub> -N	NO <sub>3</sub> -N	NO <sub>3</sub> -N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	NO <sub>3</sub> -N
L/F	G1	1	48	26	54	11	25	65	46	1.5	30	4.9	UD	UD	3.7	UD	
	G2	2	56	28	73	11	22	58	47	1.5	31	1.9	UD	UD	1.4	UD	
	G3	3	69	21	46	12	11	35	22	0.9	25	1.3	UD	UD	1.6	UD	
	G4	4	69	18	64	16	17	52	34	1.3	26	2.8	UD	UD	3.3	UD	
	G5	5	86	23	72	17	21	57	44	1.6	28	1.6	UD	UD	2.0	UD	
	G6	6	75	28	70	12	29	62	52	1.6	32	3.1	UD	UD	UD	UD	
	G7	7	143	15	93	22	14	40	26	1.0	27	3.6	UD	UD	2.8	UD	
	G8	8	70	29	71	21	26	58	53	1.4	39	0.7	UD	UD	UD	UD	
	G9	9	56	24	57	13	24	66	46	1.7	28	1.4	UD	UD	UD	UD	
	G10	10	53	21	61	12	19	68	48	2.0	24	4.9	UD	UD	2.1	UD	
	G11	11	37	23	54	16	19	70	44	1.7	27	2.5	UD	UD	2.1	UD	
	G12	12	51	25	61	12	19	73	51	1.9	28	3.4	UD	UD	1.9	UD	
	G13	13	28	26	39	11	18	63	40	1.6	25	3.0	UD	UD	1.5	UD	
	G14	14	32	20	50	13	20	75	50	2.2	23	7.7	UD	UD	5.4	UD	
H	G1	1	23	19	29	9	25	66	36	1.4	26	2.3	UD	UD	2.2	UD	
	G2	2	38	26	59	8	21	44	23	1.0	24	1.7	UD	UD	1.6	UD	
	G3	3	35	10	28	7	11	34	17	0.8	21	1.0	UD	UD	0.6	UD	
	G4	4	34	10	31	9	12	35	20	0.8	24	1.7	UD	UD	2.2	UD	
	G5	5	61	16	55	15	14	28	17	0.7	24	1.4	UD	UD	0.9	UD	
	G6	6	54	25	49	14	47	83	43	2.0	22	3.5	UD	UD	0.6	UD	
	G7	7	50	7	47	11	9	20	12	0.5	24	1.4	UD	UD	2.0	UD	
	G8	8	59	21	84	26	28	130	53	1.8	30	0.9	UD	UD	0.7	UD	
	G9	9	37	21	46	15	34	79	43	1.9	23	1.7	UD	UD	1.8	UD	
	G10	10	21	12	20	8	15	44	24	1.1	21	3.9	UD	UD	1.4	UD	
	G11	11	20	16	27	12	21	68	34	1.6	22	1.5	UD	UD	1.2	UD	
	G12	12	27	19	37	12	31	90	45	2.1	22	4.9	UD	UD	8.0	UD	
	G13	13	19	18	25	10	19	60	35	1.6	21	5.5	UD	UD	1.5	UD	
	G14	14	16	14	21	10	26	91	46	2.2	21	5.5	UD	UD	2.5	UD	



### Water

The water chemistry with regards to eutrophication and acidification parameters is presented in **Table 5.3.4**. Where possible, the results are classified according to the EUs Water Framework Directive (WFD). In the WFD a water body is assessed with respect to chemical and ecological status. First the water body is classified into a water type, and measured quality elements (e.g. pH, concentrations of nutrients, abundance of fish etc.) are further classified into five status classes: high, good, moderate, poor and bad, based on given values for each element and type of water body.

High
Good
Moderate
Poor
Bad

**Figure 5.3.2** The WFD classification scheme for water quality includes five ecological status classes: high, good, moderate, poor and bad.

In this classification system “high status” is defined as a condition with no or very low human pressure. The general objective of the WFD is to achieve “good ecological status” for all surface waters by 2015. Classification of ecological status is based upon the status of the biological, hydromorphological, and physio-chemical quality elements. A limited number of physio-chemical quality elements have been assessed in this report. The overall ecological status of the lakes is not provided. Classification is performed according to Veileder 01:2009 (Direktoratsgruppa Vanndirektivet, 2009). For some of the quality elements analysed in this report, class boundaries have not yet been set in the WFD. In these cases the Norwegian classification system can be applied. This system is based on similar principles as the WFD, with five status classes (Andersen et al. 1997).

**Table 5.3.4** shows that lakes M5, M6, M9, M11, M12, M13, M14, M16, M19, and M54 have elevated concentrations of Tot-N and/or Tot-P, and do not achieve “good status” according to WFD-classification. In the process of eutrophication of lakes Tot-N and TOT-P are key parameters. Elevated concentrations of Tot-N and/or Tot-P in lakes are often linked to agricultural run-off, either due to fertilizer use, animal husbandry and pasture-land, or untreated sewage effluent from household. All lakes except M16 have various agricultural activities in their catchments. Increased levels of Tot-N and Tot-P in these lakes are most likely due to leakage from farming activities. Lake M16, situated at island Fedje, also had elevated concentrations of Tot-P. The lake is situated at the west coast of the island in a boggy and pristine area about 2.5 km from the North Sea, without agriculture or houses in the catchment. The Fedje island has a dense population of deer, and the West Coast of the island is recognized for a high population of migratory birds. Animal manure from birds and deer might explain the elevated Tot-P concentration in the lake.

Increased emissions and deposition of nitrogen can lead to acidification of surface water. Most N is usually retained in soil and vegetation in the catchment (and thus leads to nutrient enrichment of the terrestrial ecosystem). Nitrate is a mobile strong acid anion and is accompanied by equivalent amounts of cations, like hydrogen, aluminium, calcium and magnesium will then be transported to the lake. The nitrogen that leaves the catchment in runoff in the form of nitrate and accompanied by acid cations such as H<sup>+</sup> and inorganic Al (LAI) contributes to lake acidification. Similarly inorganic N deposited directly on the lake surface can add to acidification. Acid neutralising capacity (ANC) is a

measure of the acidification status of water. ANC is defined as the equivalent sum of base cations (Ca, Mg, Na, K) minus the equivalent sum of strong acid anions ( $\text{SO}_4$ ,  $\text{NO}_3$ , Cl). ANC levels above about  $20 \mu\text{eq L}^{-1}$  indicate water quality suitable for fish populations such as brown trout. As shown in **Table 5.3.4** several lakes are acidified by this measure as they have low ANC (M01, M02, M03, M08, M10B, M16, M18, M29, M20, M21, M28, M, 52, and M53). In all these lakes, except M52 low pH and reduced alkalinity are measured as well, indicating that the lakes are sensitive to acid deposition.

Chemical analyses from the remaining lakes M17, M24, M26, M29, M31, M32, M33B, M50, and M51 indicate that the lakes are less sensitive to acidification. They are localized in pristine areas with minor human pressure. Levels of TOC and pH vary between the lakes, mainly due to influence of humic material, representing lakes of oligotrophic and dystrophic character.

Some of the results are presented on maps in appendix 10.9.

**Table 5.3.4** Major surface water chemical parameters. Colours indicate environmental quality status according WFD or Norwegian classification scheme. Columns not coloured indicate that quality elements are not classified.

Station	pH	KOND mS m <sup>-1</sup>	ALK mmol l <sup>-1</sup>	Tot-P/L µg P l <sup>-1</sup>	Tot-N/L µg N l <sup>-1</sup>	NH4-N µg N l <sup>-1</sup>	NO3-N µg N l <sup>-1</sup>	TOC mg C l <sup>-1</sup>	Cl mg l <sup>-1</sup>	SO4 mg l <sup>-1</sup>	A/R µg l <sup>-1</sup>	A/I/I µg l <sup>-1</sup>	LAI	Ca mg l <sup>-1</sup>	K mg l <sup>-1</sup>	Mg mg l <sup>-1</sup>	Na mg l <sup>-1</sup>	ANC µeq l <sup>-1</sup>
M01	5.23	3.03	0.033	3	300	5	60	4.7	6.2	1.38	61	44	17	0.26	0.15	0.43	3.52	-2
M02	5.4	1.89	0.039	11	340	4	6	5.7	3.31	0.94	65	53	12	0.21	0.23	0.22	2.26	19
M03	5.23	2.48	0.035	3	280	12	45	5.4	4.57	1.4	98	73	25	0.34	0.16	0.33	2.81	9
M05	6.14	4.32	0.079	27	500	<10	46	11.7	7.43	2.26	80	80	0	1.52	0.54	0.64	4.89	95
M06	4.7	3.78	0.016	9	525	5	2	20.8	5.87	0.81	34	37	0	0.46	0.03	0.64	3.83	61
M08	5.33	3.02	0.037	13	370	9	65	5.5	6.04	1.42	52	43	9	0.36	0.4	0.43	3.47	10
M09	5.69	1.61	0.054	28	300	16	<1	5.8	1.85	1.43	34	30	4	0.71	0.38	0.26	1.42	46
M10B	5.18	1.33	0.033	5	255	3	11	5.4	1.67	0.93	88	69	19	0.19	0.1	0.14	1.35	15
M11	6.15	3.2	0.115	48	605	<2	41	16.1	3.74	1.8	93	88	5	2.16	0.52	0.64	3.18	166
M12	6.38	3.43	0.106	87	710	26	145	10.8	4.57	1.83	84	77	7	1.89	1	0.61	3.18	131
M13	6.46	3.82	0.111	27	530	<10	56	9	5.51	2.47	55	51	4	2	0.7	0.69	3.73	126
M14	5.54	4.53	0.055	18	485	<2	40	13.1	8.51	2.41	69	63	6	1.03	0.34	0.83	5.24	63
M16	5.18	7.48	0.04	16	415	<20	9	12.2	17.7	2.28	23	21	2	0.61	0.41	1.19	10	27
M17	6.47	5.34	0.07	5	310	<10	75	3.6	12	2.29	13	13	0	1.33	0.25	0.9	6.41	34
M18	5.55	1.33	0.04	5	215	2	28	3.6	1.93	1.01	58	47	11	0.22	0.12	0.15	1.5	14
M19	5.89	1.33	0.045	12	205	9	35	2.6	1.91	1.22	41	32	9	0.6	0.18	0.19	1.3	25
M20	5.25	1.43	0.031	3	215	7	75	2.1	2.37	0.81	49	31	18	0.1	0.08	0.16	1.42	-7
M21	5.73	1	0.042	3	160	<2	23	2.6	1.35	0.79	51	42	9	0.28	0.08	0.13	1.11	19
M24	6.24	3.8	0.059	8	355	10	110	3.8	7.57	2.12	32	28	4	0.98	0.41	0.65	4.25	33
M26	6.39	3.43	0.07	4	290	4	78	3	6.67	1.92	28	23	5	1.05	0.18	0.56	3.96	42
M28	5.91	0.75	0.04	2	155	7	30	1.2	1.19	0.49	16	13	3	0.13	0.07	0.1	0.83	7
M29	6.58	1.06	0.071	2	160	8	30	1.6	1.06	0.61	28	25	3	0.88	0.09	0.1	0.86	47
M31	5.67	2.9	0.053	7	445	8	170	9.2	4.93	1.29	133	115	18	0.92	0.57	0.44	3.04	51
M32	5.83	1.96	0.048	4	235	5	24	5	3.38	1.31	35	34	1	0.63	0.22	0.31	2.08	29
M33B	5.94	1.45	0.05	9	250	17	17	4.3	2.35	0.75	43	39	4	0.36	0.18	0.24	1.56	27
M50	6.32	4	0.074	10	330	<10	7	6.8	7.63	2.08	35	35	0	1.07	0.3	0.62	4.83	63
M51	6.52	3.74	0.09	10	375	<2	83	4.9	6.64	2.04	30	27	3	1.63	0.64	0.63	3.77	78
M52	5.87	6.96	0.046	6	240	<20	16	4	16.6	2.83	33	29	4	0.75	0.42	1.07	9.05	2
M53	4.85	1.74	0.022	4	265	<2	2	7.9	2.23	0.52	91	81	10	0.21	0.11	0.19	1.41	16
M54	6.72	4.53	0.138	13	575	17	215	5.7	7.01	2.32	28	25	3	2.82	1.03	0.63	4.07	135

### 5.3.2 Amines/nitramines/nitrosamines

#### Amines

Amine concentrations in samples of soil, plants and water are presented in **Table 5.3.5**.

**Table 5.3.5** Concentrations of amines analysed in the samples. Values for soil and plants are given per gram fresh (frozen) material.

Plot	Methyl amine (MA)	Ethylamine (EA)	Dimethyl amine (DMA)	Diethyl amine (DEA)	Monoethanolamine (MEA)	2-Amino-2-methylpropanol (AMP)	Piperazine (PIP)
Soil (ng g <sup>-1</sup> )							
1	88	<1	515	<1	188	<1	<1
2	91	<1	360	<1	155	<1	<1
3	17	<1	125	<1	292	<1	<1
4	90	4	220	22	174	<1	<1
8	62	8	239	684	102	<1	<1
10	77	9	365	106	71	<1	<1
11	76	7	453	69	228	<1	<1
13	47	4	405	58	242	<1	<1
Moss (ng g <sup>-1</sup> )							
1	39	13	693	<1	445	61	<1
2	26	<1	768	477	534	36	<1
3	27	4	553	<1	527	38	<1
4	63	9	857	143	400	21	<1
8	102	9	552	626	338	148	<1
10	62	6	935	<1	431	26	<1
11	39	3	663	<1	498	2	<1
13	105	17	989	57	318	55	<1
Water (ng L <sup>-1</sup> )							
M02	3 587	<10	25 719	<10	343	<10	<10
M08	3 252	<10	23 834	18	650	<10	<10
M11	6 727	<10	49 081	<10	415	<10	<10
M16	8 601	<10	42 969	71	351	<10	<10
M33b	2 146	<10	15 606	56	232	<10	<10
M50	2 065	<10	22 190	35	245	124	<10
M51	1 892	<10	14 386	31	353	<10	<10
M52	1 501	<10	11 160	<10	401	178	<10
M53	8 694	<10	41 889	86	<10	327	<10
M54	2 031	<10	16 810	26	378	502	<10

MA, DMA and MEA were detected in all soil, moss and water samples, only one water sample was below the LOD for MEA. EA, DEA and AMP were detected in some samples, while PIP was not detected in any samples. In general, the level of DMA and MEA in soil and moss were 0.1-1 µg g<sup>-1</sup>, while MA and AMP were below 0.1 µg g<sup>-1</sup> in soil (this compound was not detected in moss). EA was in general below 0.01 µg g<sup>-1</sup>. In water, the highest levels of amines were noted for DMA with levels ranging from 11-49 µg L<sup>-1</sup>, while the levels of MA were 10-fold lower. The levels of MEA and AMP when detected were in general in the same range; 100-650 ng g<sup>-1</sup>, and DEA was below 100 ng g<sup>-1</sup> when detected. EA and PIP were not detected above the LOD in any water samples. The geographical information about distribution of levels of four of the amines is given in Appendix 10.10.

#### Nitramines and nitrosamines

The samples were analysed for 9 nitrosamines and 5 nitramines (**Table 5.3.6**). All the analytes were below the indicated LOD.

**Table 5.3.6** Limits of detection (LOD) for nitramines and nitrosamines analysed in the samples

<i>Nitramines</i>	<i>LOD soil/moss ng g<sup>-1</sup></i>	<i>LOD water ng L<sup>-1</sup></i>	<i>Nitrosamine</i>	<i>LOD soil/moss ng g<sup>-1</sup></i>	<i>LOD water ng L<sup>-1</sup></i>
N-Nitro-methylamine	2	1.5	Nitrosodimethylamine	1	0.7
N-Nitro-dimethylamine	2	1	Nitrosodiethylamine	1	0.7
N-Nitro-ethanolamine	2	0.8	N-nitrosodiethanolamine	1	1.1
2-methyl-2-nitroamino-propanol	2	0.7	Nitroso-N-methylethylamine	1	0.7
N-Nitro-piperazine	2	0.9	Nitroso-N-propylamine	1	0.7
			Nitrosomorpholine	1	0.7
			Nitrosopyrrolidine	1	0.7
			Nitrosopiperazine	1	0.7
			Nitrosopiperidine	1	0.7

### 5.3.3 Analytical screening

#### *Gas chromatography/time-of-flight/mass spectrometry (GC-ToF-MS)*

The extracts were analysed by the instrument operated in full-scan positive-electron impact mode (m/z 50-800). The mass spectra were deconvoluted using Micromass software (MassLynx V4.1, ChromaLynx) and compared with reference spectra in the National Institute of Standards and Technology (NIST) mass spectral database for tentative identification. In addition, accurate mass spectra to 4 decimal places were used for peak identification with error thresholds of 5 and 50 mDa for high and low precision mass tolerance, respectively. This combination of identification criteria ensures a more secure identification process.

The raw data as well as the deconvoluted data with tentative identifications were saved and will be stored for a period of 5 years. Examples of chromatograms of moss (G2), soil (G3) and water (M23) both underivatized and derivatized are shown in Appendix 10.13. In general the figures show 4 different windows from the identification program (Chromalynx XS Identify V 4.1)

- The chromatogram: the chromatogram is given in the top window. The blue triangle in the top show the position of the compound for which the details in the other windows give more information. The triangles on the bottom show where the software has identified compounds with different mass spectra. The colour of the triangle represents the match factor given to each compounds mass fragmentation pattern in comparison to the NIST library. A match factor of 1000 is given for a perfect match. The green triangles are for compounds with a match factor above 800, the yellow colour between 600 and 800, and red triangles for match factors below 600.
- The Compound window shows a list of all the tentatively-identified compounds in the chromatogram, with details regarding retention time, abundance etc.
- The spectrum window gives a comparison between the mass spectrum of the compound in question (lower part) and the reference spectrum from the NIST library (upper part).
- The library match window gives information about the different identifications suggested for each compound in the chromatogram (10 suggestions for each compound). The upper compound has the highest match factor and the highest probability. Details are given for each compound e.g. molecular weight, match factor and CAS number. The accurate mass scoring (given in mDa inaccuracy from the target mass) gives details for the 10 most intense fragments in the mass spectrum.

In general, the chromatograms for moss and soil show a larger abundance of compounds than do those for water. The derivatization with BSTFA results in a visible hump, which is largely due to the derivatization process. The rationale for derivatization of the sample is that compounds with a

reactive function, such as OH or NH will react with the derivatising agent, and consequently be more volatile with a higher and therefore more easily detected mass. However, derivatisation makes the deconvolution process less suitable for identification processes, since few of the compounds in the NIST library are derivatives. Since the purpose of the screening process was storage of data, the effort has not been devoted to the task of identifying individual compounds.

Compounds that have no reactive group will be present in both the underivatised as well as in the derivatised sample, as the chromatograms in Appendix 10.13 show. In the moss sample, hexadecane with an Rt of 8.85 min is present in both the underivatised as well as in the derivatised sample. The match factor is quite high in both extracts, and accurate mass scoring confirms the identification. The same is also shown for tricosane in soil and eicosane in the water sample. These are all naturally-occurring fats.

#### *Liquid chromatography/mass spectrometry (LC-MS-MS)*

The raw data from both the underivatised as well as the derivatised samples were saved and will be stored for a period of 5 years. The chromatograms from the LC-MS-MS are not shown in the report.

In general, the usefulness of the screening of compounds is that the data can be compared to extracts in later monitoring studies. Future screening should if possible make use of passive sampling techniques for water sample in order to accumulate more compounds from water in which the concentrations of compounds can be very low. Passive sampling technique would offer better opportunities for sampling more compounds of interest in the water phase, and the technique can be used with both target chemical analyses as well as screening methods. We therefore suggest that screening methods should be considered in the monitoring program.

## 6. Proposal for monitoring program

This programme for monitoring the natural environment after start-up of the TCM operations is based on the measurements conducted under the baseline study. The programme is designed to monitor possible changes due to three separate pollution issues: eutrophication (nutrient enrichment), acidification, and risk of toxic effect of amines, nitrosamines and nitramines. The receptors chosen were the same as in the baseline study: terrestrial vegetation, soil and surface water.

Such a monitoring programme could be quite flexible, and the level of effort made to reflect the actual emission levels from TCM, and the risk of environmental effects of these emissions. If changes in eutrophication and acidification due to N emissions are to be monitored, for example, then a minimum volume of measurements (both in time and space) must be undertaken, such that the results give clear statistically-significant answers.

The terrestrial monitoring need not begin until 6 months after commencement of operations at TCM; terrestrial monitoring will be conducted in summer/early autumn). The aquatic benthic algae sampling (yearly each August) need not begin until 6 months after commencement of operations at TCM. The lake sampling for chemical analyses should begin 3 months after commencement of operations at TCM.

### 6.1 Terrestrial ecosystem measurements

#### ***Annually***

Field inspection of condition of all 14 vegetation sites and 8 forest sites (fire, logging etc).  
Alternating sampling of pairs of 4 of the 8 A/N/N-plots every second year.

#### ***Every second year***

##### Ground vegetation

Reanalysis of the 8 (of 14) A/N/N-sites (sites at which in the baseline study samples were taken for analysis of A/N/N).

##### Trees

Tree vitality (pine) and needle chemistry analysis to be determined at 4 (of 8) fixed sites in a gradient of distance from Mongstad. Algal growth on bark of birch trees determined at the same 4 sites.

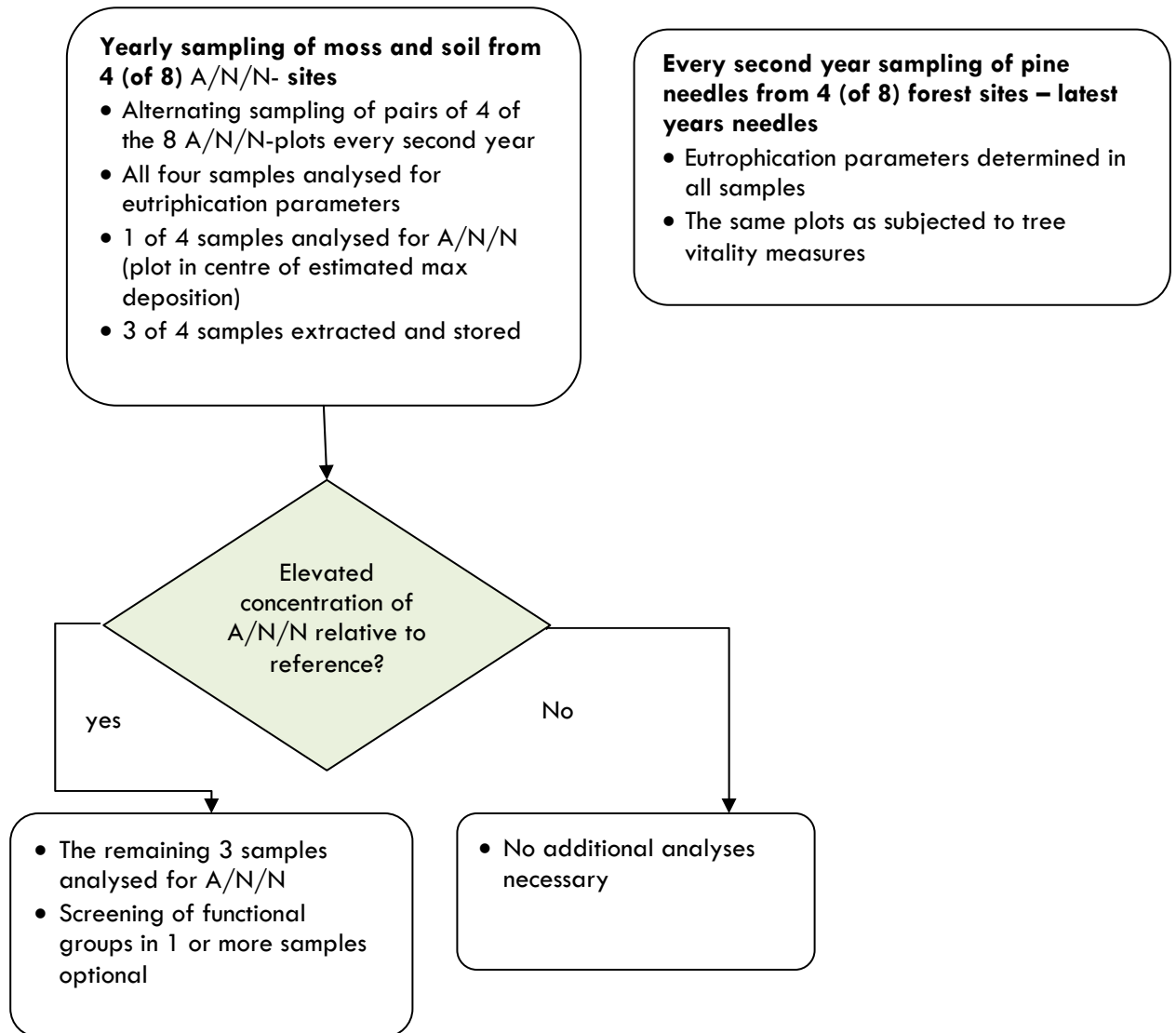
#### ***Year 5 of operation of TCM***

Repeat of baseline study. Complete new determination of all parameters at all the sites for both vegetation and trees, including leaf area index (LAI) and new growth measurements of pine trees. See Figure 6.2.2 for details.

## 6.2 Terrestrial – chemical analyses

The chemical measurement program is shown in

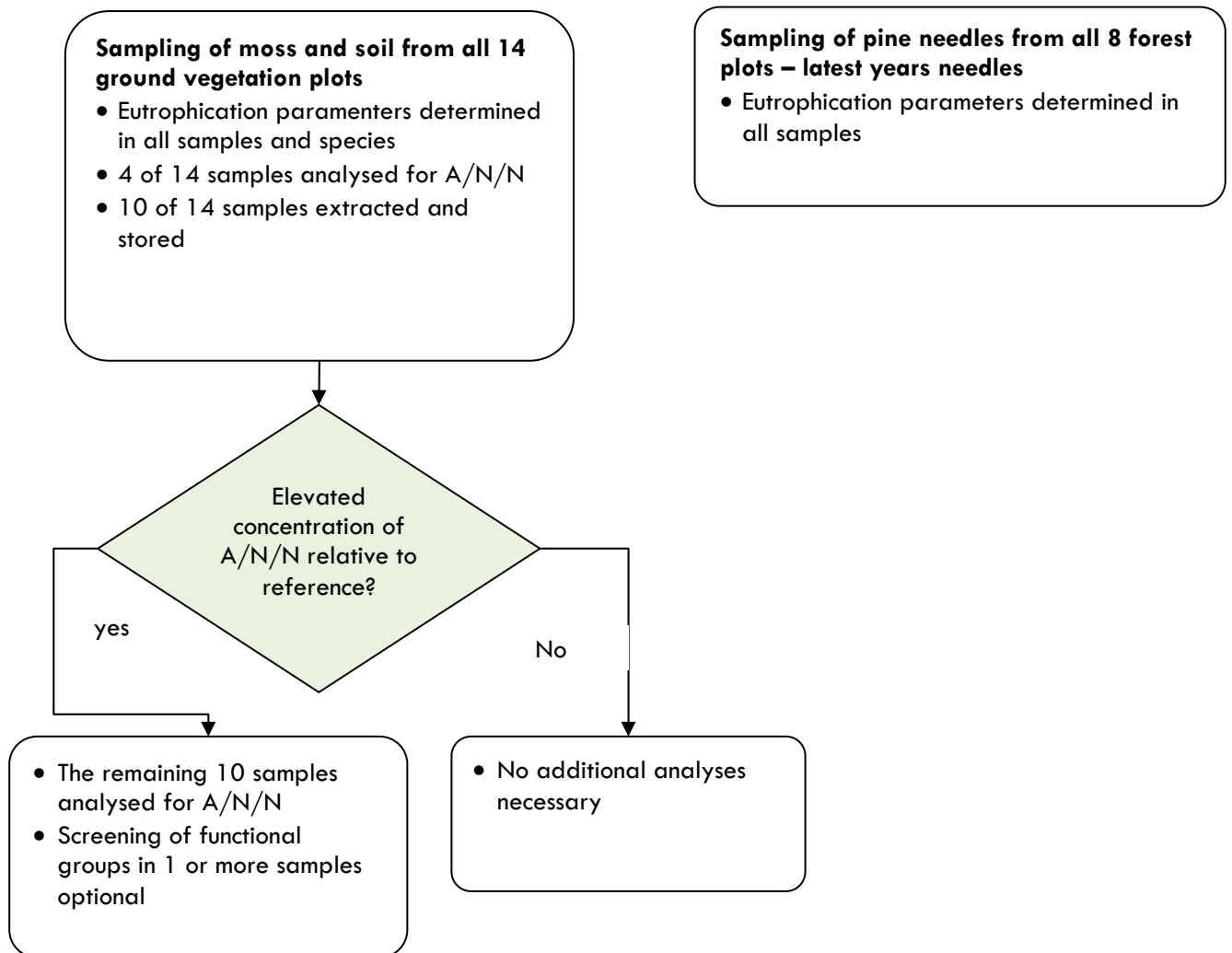
**Figure 6.2.1**, and more details in **Table 6.4.1**. A/N/N analysis of moss and soil will be done annually in at least one sample, and needle chemistry analysis will be done in four samples every second year.



**Figure 6.2.1** Chemical analyses of terrestrial matrices



**Year 5 of operation of TCM**



**Figure 6.2.2** Chemical analyses of terrestrial matrices after 5 years of operation of TCM

### 6.3 Aquatic ecosystem measurements

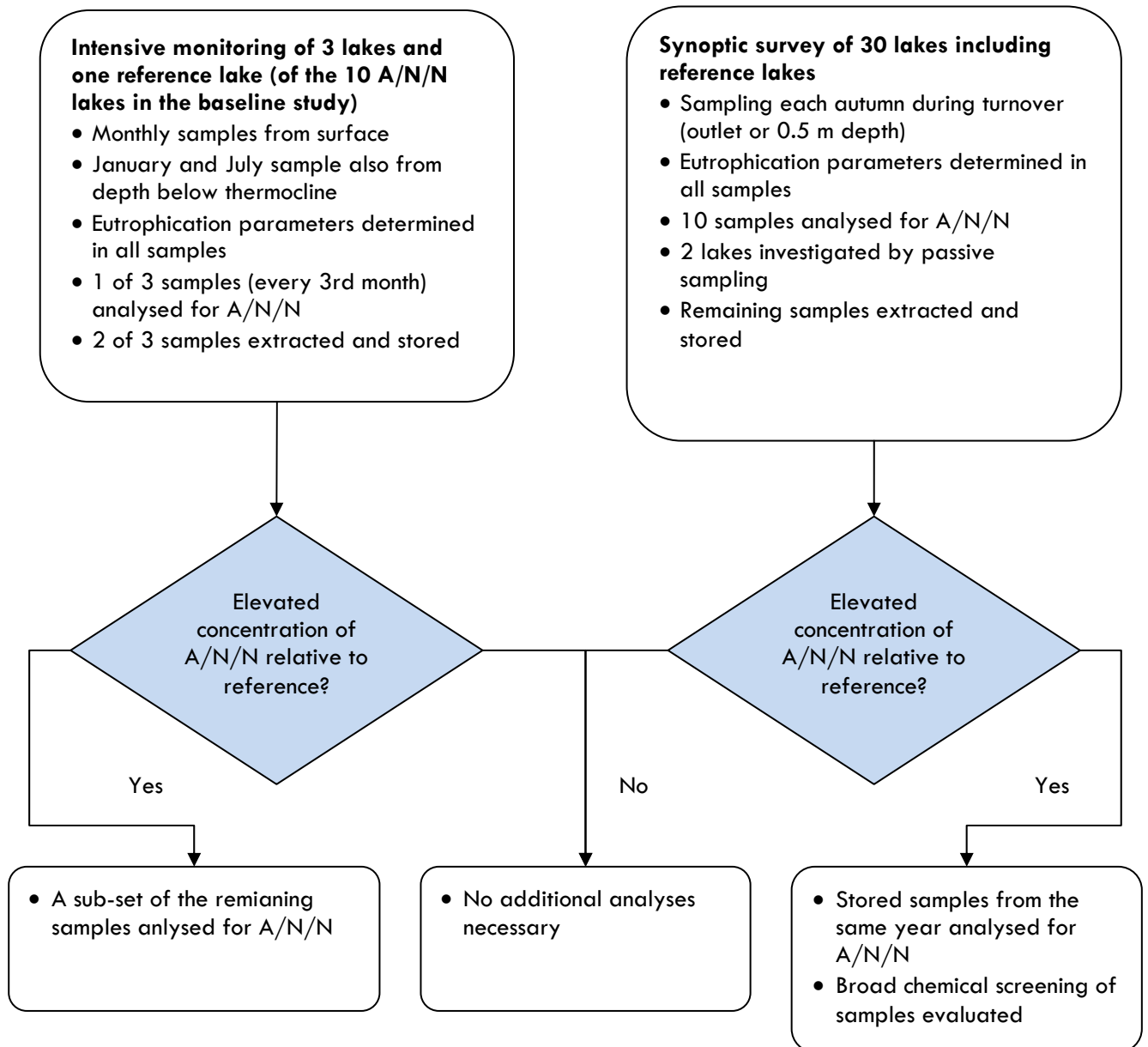
**Annually**

Benthic algae from the 10 sites of the baseline study sampled in August/September and determined to species level for calculation of PIT and AIP indices.

### 6.4 Aquatic – chemical analyses

**Annually**

The proposed monitoring scheme is depicted in **Figure 6.4.1** and **Table 6.4.1**.



**Figure 6.4.1** Annual chemical analyses of aquatic matrices.

**Table 6.4.1** Time schedule of the proposed annual monitoring

Activity	Yearly (or * Every second year)												Number of samples for analysis/storage		
	Jan	Feb	Mars	April	May	June	July	Aug	Sept	Oct	Nov	Dec	Eutrophication	A/N/N	Preparation/Storage
<b>Ecosystem measurements</b>															
<b>Terrestrial ecosystem</b>															
Ground vegetation – species composition							8 sites *								
Trees - vitality							4 sites *								
<b>Aquatic ecosystem</b>								10 stations							
Benthic algae															
<b>Chemical analyses</b>															
<b>Terrestrial – soil</b>															
Eutrophication analyses							4 sites						4		
A/N/N analyses							1 (3)							1	3
<b>Terrestrial – moss</b>															
Eutrophication analyses							4 sites						4		
A/N/N analyses							1 (3)							1	3
<b>Terrestrial – pine needles</b>															
Eutrophication analyses							4 sites *						4		
<b>Aquatic – surface water</b>															
Eutrophication analyses	8	4	4	4	4	4	8	4	4	30	4	4	82	15	61
A/N/N analyses	2(6)	(4)	(4)	1(3)	(4)	(4)	2(6)	(4)	(4)	10 (20)	(4)	(4)		2	
Passive sampling – A/N/N analyses										2					
<b>Sum analyses</b>													94	19	67

Numbers in parenthesis are samples that will be extracted (in the case of water) and stored

## 7. Discussion

### 7.1 Terrestrial ecosystem measurements

#### 7.1.1 Ground vegetation

Atmospheric nitrogen deposition has been a concern with regard to general eutrophication effects, also in semi-natural habitats such as coastal heathland (Bobink et al. 1998, Emmett 2007, Van Landuyt et al. 2008). The species composition and distribution of the *Calluna* dominated heaths investigated suggest that the vegetation in general is associated with low nitrogen availability (**Figure 5.1.1**). This corresponds well with results from other studies in the region (Øvstedal 1985, Aarrestad & Vandvik 2000). Therefore, the *Calluna* heath dominated vegetation is susceptible to additional nitrogen which will influence both abundance and composition of species due to differentiated species responses. Several studies, both experimental and field studies, have shown a transition from *Calluna* dominated heaths towards a higher dominance of grass species, such as *Molinia caerulea* and *Deschampsia flexuosa*, following N fertilisation (Fremstad 1992, Bobink et al. 1998, Power et al. 1998, Britton et al. 2003, Barker et al. 2004, Edmondson et al. 2010). Thus, the species having the potential to take advantage of increased nitrogen levels will become more dominant and gradually outcompete the *Calluna* heaths.

The nitrogen deposition level at which such coastal heathlands may deteriorate is estimated to be within the range of 15 to 20 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Heil and Bobink 1993a, b), depending on local moisture conditions. The wetter heathlands tolerate more than the dryer sections, approximately 17-22 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Berendse 1990). A critical load for transitions of heathlands into more grass dominated vegetation in Norway has been recognized in the range of 10 to 20 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Aarrestad et al., 2010). The investigated region includes both wet and dry heathlands, and a wet-dry gradient is also present within the individual sites.

For Lindås the background nitrogen deposition in the range 8 to 10 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Berglen et al. 2010). It is questionable whether the terrestrial eutrophication indicators are sufficiently sensitive to respond to the expected additional N deposition from TCM of about 0.03 kg N ha<sup>-1</sup> yr<sup>-1</sup> (c. 0.3% increase) (Berglen et al. 2010). The worst case scenario for wet deposition from the TCM is an additional 0.7 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Berglen et al. 2010), which may seem minor in comparison to present levels. However, the total deposition level may then reach about 11. kg N ha<sup>-1</sup> yr<sup>-1</sup>, which is in the lower range of the critical load, and within the range suggested for Norwegian heathland deterioration (Aarrestad et al., 2010). Thus, increased nitrogen deposition associated with the worst case emission scenario may accelerate vegetation changes in the Lindås area.

According to redlist of nature types the three major threats to deterioration of coastal Calluna-heathlands are nitrogen deposition, farmland abandonment and increased woodland (Lindgaard & Henriksen 2011). Then, irrespective of additional nitrogen input, the vegetation in the region is changing as the management regime that maintained heathlands has more or less ceased (Aarrestad & Vandvik 2000). The abandonment of older farming traditions during recent decades, i.e. reduced fire frequency and less sheep grazing, has led to reforestation of the coastal landscape. Thus, there are multiple factors at play that may contribute to an increased rate of change in vegetation successions. These factors may make it difficult to identify changes associated with extra N-input.

### 7.1.2 Trees

All the forest sites were located in pine dominated forest in southeastern direction from TCM. Due to rather scattered distribution of forest stands, varying conditions and former human impacts, the forests condition showed a great variability. The selection of homogenous monitoring plots in cutting class III and IV was challenging and had to be adjusted to the prevailing conditions.

Forest sites F1-F4, closest to TCM, were located in rather dense, highly productive Scots pine plantations, established in the 1950s. The Hart-Becking spacing index (S%) was high, from 14 to 16, implying that these plots are approaching the self-thinning limit. Dead standing trees account for a limited proportion of the volume (<4%). The basal area was above  $40 \text{ m}^2 \text{ ha}^{-1}$  and standing volume has passed  $344 \text{ m}^3 \text{ ha}^{-1}$ . The highest volume of  $463 \text{ m}^3 \text{ ha}^{-1}$  was found at F1 (**Table 5.1.1**). Expected yield class was 6 to  $7 \text{ m}^3 \text{ ha}^{-1} \text{ yr}^{-1}$ , over rotations of 75 to 85 years. Standing volumes above  $400 \text{ m}^3 \text{ ha}^{-1}$  and yield class 7 are rare in the oceanic pine forest (Øyen & Nes 1997, Øyen et al. 2006). Due to the high density the crowns were narrow and short.

The other four sites (F5-F8) were semi-natural, rather open grown pine stands on more moderate site indices class,  $H_{40}$ -class is 11 or 14. General yield potential at such sites is  $3.5$  and  $5.0 \text{ m}^3 \text{ ha}^{-1} \text{ yr}^{-1}$ , respectively. However, the stand density was rather low, below  $26 \text{ m}^2 \text{ ha}^{-1}$ , indicating sub-optimal stocking, probably due to patchy regeneration. The field and bush layers were rather restricted at F1 and F2, but more pronounced and including *Juniper* at F3-F8.

The tree ring analysis (**Figure 5.1.2**) revealed that year-to-year variation in increment was large, with however, high correlation between adjacent sites (**Table 5.1.2**). Annual ring widths over the last 20 years typically showed a decreasing trend, and at present stage they fluctuate between 1 to slightly above 2 mm per year. F7 and F8 are at lower site index and in an earlier developmental stage than the two the other sites.

## 7.2 Aquatic ecosystem measurements

### 7.2.1 Benthic algae

#### *Assessment of the suitability of the sampling sites for monitoring purposes*

The sampling sites in the Flekke-Guddal and Yndesdal catchment have a rather stable benthic algae community, which is reflected in fairly stable PIT and AIP indices over the last years. We thus feel confident that trends, if occurring, would be detected, and that the sites are suitable for comparison with the six other sites, which may receive additional deposition of nitrogen after start-up of TCM.

All three sites north of Mongstad are oligotrophic and slightly acidic, and as such are directly comparable with the sites in Flekke-Guddal and Yndesdal. In contrast, agricultural use and probably a slightly different geology lead to more eutrophic and less acidic streams in the area south of Mongstad. One of the suggested sites south of Mongstad (LLI ISK), however, is oligotrophic. At this site, benthic algae were generally scarce (although we did find enough indicator species to enable calculation of a reliable PIT index). Nitrogen emissions from TCM could lead to increased algae biomass at this site, such that regular monitoring at this site is highly relevant.

We did not find additional suitable oligotrophic stream sites in the relevant area south of Mongstad. The two other sites (LLI IFO and LLI DAL) are more eutrophic than the other proposed monitoring sites. Though we expect that any effects of TCM, if occurring, likely first would become evident in oligotrophic sites, we do not regard it a disadvantage to include two meso-eutrophic sites. In this

way, differences between sampling sites become clearer, and future interactions between TCM and nutrient concentrations could be detected.

For the future monitoring we suggest determination of the PIT and AIP indices. In addition, we suggest application of multivariate analyses of species composition and abundance in order to detect possible trends in abundance of individual species. This type of analyses makes sense, however, only for long time data series. Regular monitoring of benthic algae in streams in the Mongstad area will allow detection of changes in species composition and abundances that might be caused by emissions to the atmosphere.

## 7.3 Chemical analyses

### 7.3.1 Eutrophication and acidification parameters

#### *Vegetation*

**Pine:** Elements such as N, K, P and Mg are readily translocatable within trees and other plants (Salisbury and Ross 1985). For that reason they are found at higher concentrations in current year needles (2010) than previous year needles (2009) (**Table 5.3.1, Figure 5.3.1**). The opposite is the case for the immobile elements such as Ca and Fe which have larger concentrations in the 2009 than 2010 needles. Na is not an essential element in plants, but is an indicator of sea salt deposition. The higher concentrations in 2009 needles are due to the longer accumulation time.

When comparing nutrient levels in the 2010 needles with the diagnostic thresholds values (Brække 1994), it is quite clear that the levels of N, K and P are sub-optimal or even deficient. Levels of Ca, Mg and S were, however, present at optimal levels. Sampling of pine foliage took place in April 2011, before onset of growth. Accordingly, the 2010 needle year class was the most recent needle class at the time of sampling. Ideally, sampling of pine foliage should take place between October and March, before the needles start accumulating carbohydrates and dry matter which reduces the relative proportion of nutrient elements (Brække 1994). Due to the late onset of the project, this was not feasible. The fact that some elements show deficiency still indicates a poor availability of N, K and P. Since access to N in forests is usually sub optimal (Stuanes and Abrahamsen 1996), pine possibly has the potential to increase growth following increased N supply. In trees, however, this response is not immediate.

**Heather, Cladonia and Hylocomium:** Concentrations of N and P in current year's shoots of heather have been shown to increase in response to high deposition rates of these elements (Edmondson et al 2010, Power and Collins 2010). The foliar N concentration in our study varied from 0.98 to 1.59 % of dry matter (**Table 5.3.2**) (i.e. 9.8-15 mg g<sup>-1</sup>), very similar to the study of Power and Collins (2010). Similarly, N concentration in Cladonia is reported to be positively correlated to N deposition (Britton and Fisher 2010), and our results varied within the range reported by Hyvärinen and Crittenden (1998). In both species, it is uncertain whether they are sufficiently sensitive to detect the likely small relative increase in N deposition expected after onset of CO<sub>2</sub> capture, as the empirical studies have taken advantage of a very big difference in deposition levels (e.g. Power and Collins 2010, Hyvärinen and Crittenden 1998). *H. splendens* has also been shown to accumulate N in accordance with atmospheric deposition, and the variation in our results reflect fairly well the range reported for Finland (Poikolainen et al 2009). The concentrations of Ca, K, Mg and P are all within the range reported by Migaszewski et al. (2011). Our sampling, however, included the entire moss segments to get enough material, not standardized to the last four annual shoots, or the shoot tips (e.g. Migaszewski et al. 2011). As for pine, the best time for sampling of heather and moss is in the dormant period. However, as pine and heather/moss were sampled in the initial and late part of the

growing season, respectively, the negative effect were minimized. For the monitoring, timing of sampling should be repeated at the same times to get comparable results.

#### *Soil*

Nitrate concentrations were at or below the detection limit in both KCl and water extracts for both soil horizons at all plots (Table 5.3.3), which is consistent with the results for ground vegetation (**Figure 5.1.1**) and suggests a low risk of nitrate leaching at present. A small relative increase in inorganic N deposition is unlikely to change this. Ammonium concentrations were generally above the detection limit. It is common that ammonium concentrations in soils are higher than nitrate concentrations: ammonium is less mobile in soil than nitrate because it binds to negatively charged soil particles. Most nitrogen was present as organic N, rather than as nitrate or ammonium. Ca and Mg inputs appear to be dominated by sea salts, and these will continue to be an important input in the future.

It is probable that some amines were determined as “ammonium”. However, the amounts involved are likely to have been small, and below the levels of uncertainty involved in the sampling and analysis.

#### *Water*

The emissions from TCM can potentially affect lakewater in 3 ways: (1) nutrient imbalance (eutrophication) due to nitrogen deposition, (2) acidification due to changes in nitrate concentrations, (3) changed concentrations of potentially toxic compounds such as amines, nitrosamines, and nitramines. Point (3) is discussed in the next chapter (7.3.2).

The emissions of amines, although in themselves basic, have the potential to undergo rapid acid-base reactions to form salt particles and form nitrate (Ge et al. 2011). To determine potential changes in acidification status (point 2), analysis of nitrogen containing compounds (tot-N, nitrate, ammonium) as well as major ions is recommended. The ions are important because the most widely accepted measure of acidification status is the acid neutralising capacity (ANC). ANC is defined as the equivalent sum of base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) less the equivalent sum of strong acid anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ). Determination of ANC thus requires measurement of these 7 ions.

Deposition of amines adds N to soil and surface water. Nitrification of reduced N compounds contributes to  $\text{NO}_3$  concentrations in soil solution and water. If nitrification occurs in soil and the resulting  $\text{NO}_3$  leaches to surface water accompanied by acidic cations such as  $\text{H}^+$  and  $\text{Al}^{\text{nt}}$ , then deposition of amines adds base to soil and acid to surface water. In the lakewaters analysed, concentrations of amines (mostly methyl- and dimethylamine) were in the range of 4-18 as  $\mu\text{g N L}^{-1}$ . This range is similar to that of  $\text{NH}_4\text{-N}$  concentrations in these 10 lakes ( $<2 - 17 \mu\text{g N L}^{-1}$ ), whereas  $\text{NO}_3\text{-N}$  levels were higher (2-215  $\mu\text{g N L}^{-1}$ ) and total N levels much higher (240-605  $\mu\text{g N L}^{-1}$ ). These data indicate that amines contribute a few percent of the total N content in these lakes. The source of these amines may be from atmospheric deposition and/or from organic sources within the catchment and lakes themselves.

Results from the baseline survey show that the monitoring program encompasses a combination of acid sensitive, eutrophic, and pristine surface waters. Oligotrophic, meso/eutrophic, and dystrophic lakes have been included in the monitoring programme in order to cover various trophic classes of surface waters.

Several of the lakes have previously been monitored, and results show that these lakes are still acidified, although the situation has improved since 1988-1992. Elevated concentrations of tot-P and

tot-N were found in a number of lakes, mainly due to agricultural activity in the catchment area. Pristine lakes, showing minor influence of human activity were included in the monitoring programme. Three of the lakes are used as a drinking water sources.

Altogether, we consider that the lakes selected for the monitoring programme will cover potential eutrophying and acidifying effects of deposition after start-up and operation of TCM.

### 7.3.2 Amines/nitramines/nitrosamines

MA, DMA and MEA were detected in all soil, moss and water samples (**Table 5.3.5**), and the amines may interfere with our spectrophotometric method for quantification of  $\text{NH}_4$  in soil. The amounts of the amines in soil are, however, negligible compared to  $\text{NH}_4$  (Table 5.3.3 vs. Table 5.3.5), suggesting that this method does not unduly influence the results for  $\text{NH}_4$ -levels.

According to a review by Smith (1971), aliphatic amines are widely distributed amongst the lower and higher plants. In fungi and flowers of higher plants, volatile amines frequently function as insect attractants, but in many other species their function is not understood. According to Smith (1971), typical sources for methylamine and ethylamine are *Mercurialis* (leaves) and *Malus* (fruit) respectively, while the occurrence of MEA is widespread.

Many of the selected amines have previously been detected in in the atmosphere (Ge et al. 2011) as well as in natural sources. Information from TOXNET (US National Library of Medicine) and other references are summarised below.

#### *Methylamine (MA)*

Methylamine occurs naturally. MA comes from the volatilisation of cattle waste and from decomposing fish. Methylamine occurs in herring brine, dog urine and in certain plants. It is also found in a variety of vegetables and other foods.

#### *Dimethylamine (DMA)*

Dimethylamine naturally occurs in many foods, and is volatilised from animal waste. It is also found in many plants. Dimethylamine was detected in 8 rivers in Germany at a maximum concentration of  $11.9 \mu\text{g L}^{-1}$ . It has been identified, but not quantified in uncultivated loamy soil from the Moscow region. It is possible that the amines are formed naturally rather than resulting from contamination or as a metabolite of a fertiliser or a pesticide. Dimethylamine has been detected in marine algae, and in tobacco leaf ( $4\text{-}75 \mu\text{g g}^{-1}$ ).

#### *Diethylamine (DEA)*

Diethylamine occurs naturally in many foods and plants. It has been detected in 8 rivers in Germany at a maximum concentration of  $14 \text{ ng L}^{-1}$ . It has been identified, but not quantified in volatiles from a cattle feedyard, the exhaust from a gasoline engine, furniture coatings and textile floor coverings. It has been detected in many foods, and in tobacco leaf in a concentration of  $0.1\text{-}35 \mu\text{g g}^{-1}$ . It has also been identified, but not quantified in plants from Africa.

#### *Ethanolamine (MEA)*

MEA has been identified as a normal constituent of mammal and human urine. In addition to its use as a gas scrubber, it is used as a chemical intermediate, in dry cleaning and textiles treatment, hair products and in pharmaceutical formulation. Consequently, it may enter the environment via waste water. It is also in use as a dispersing agent for agricultural chemicals, and may therefore be a result



of direct release to the environment. MEA has been identified in marine and freshwater algae, and in smoke from charring/burning of chitin (Simoneit et al. 2000).

A more detailed description of environmental occurrence of dimethylamine in water can be found in (Landesumweltamt Brandenburg 2003). In a report of the occurrence of amines in German rivers (Sacher et al. 1997), DMA was found up to  $3 \mu\text{g L}^{-1}$  in the Rhine, and MA and morpholine were found at a concentration of about  $1 \mu\text{g L}^{-1}$ . In the Elbe, the concentrations of both MA and DEA were about  $2 \mu\text{g L}^{-1}$ .

In a study of primary and secondary amines, Neurath et al. (1977) reported that 40 primary and secondary amines had been detected in samples of various natural origins, including foods and surface waters. In general, secondary amines were found in concentrations below  $10 \mu\text{g g}^{-1}$ , but higher concentrations occurred in herring preparations, some cheese and radish. DMA and DEA were the most prevalent secondary amines. MEA was not one of the analytes investigated in Neurath's study (1977).

In a recent study by Wang et al. (2011) the occurrence of nine nitrosamines and secondary amines in source water and drinking water was investigated. Six nitrosamines were detected in the samples, and the highest level of nitrosamines observed was  $42 \text{ ng L}^{-1}$  (total nitrosamines in source water) and  $26 \text{ ng L}^{-1}$  (finished water samples). DMA and DEA were the amine compounds with highest detection frequency in water samples. The levels ranged from 0.2 to  $3.9 \mu\text{g L}^{-1}$  for DMA and 0.3- $2.4 \mu\text{g L}^{-1}$  for DEA. In a report of secondary amines in river water and sediment samples, a range of amines was reported (Akyüz and Ata 2006). The level of amines was in general low ( $0.3\text{-}700 \text{ ng L}^{-1}$ ), and PIP was the amine detected in highest concentrations, both in river water and in sediments. MEA was not analysed in these two reports (note that MEA is often used as an abbreviation for methylethylamine as well).

The amine levels detected in the moss samples were in the same range as those reported in the literature for other plants. Amine levels in soil have not to our knowledge been reported previously, but not surprisingly the levels are roughly the same as reported for plant materials. The levels found in the lakes in the Mongstad area, however, were higher for DMA and MA than those reported from the few previous studies in Germany. The levels reported earlier were in drinking water and river water, and are therefore not necessarily comparable to lake water. One of the known sources for amines is animal urine. The data for eutrophication parameters such as tot-P and TOC from the lakes suggest that a few of the lakes sampled were influenced by agricultural activities in the catchment.

A simple principal component analysis (PCA) was performed with varying number of components included (Appendix 10.11). Based on these initial PCA findings, scatterplots of the five amines detected in lake water were therefore plotted against TOC, pH, Tot-N, and tot-P (Appendix 10.12). The strongest correlation was found between DMA and TOC, and to a lesser extent between MA and TOC. The other amines did not correlate with TOC. A tendency to a negative correlation was observed for the three amines MA, DMA and possibly DEA. The correlations between the amines and tot-N and tot P were quite weak.

However, DEA, MEA and AMP were not correlated with TOC. AMP has not been analysed in previous environmental samples to our knowledge. Therefore, it can be speculated that the origin of the AMP may be anthropogenic, and possibly also some of the MEA. In Ge et al. (2011) the only source given for AMP (in Ge's article referred to as isobutanolamine) is  $\text{CO}_2$  capture. Since  $\text{CO}_2$  capture has not started yet, there must be other natural or anthropogenic sources.

In conclusion, the levels of amines detected in moss and soil seemed to be in line with what has been reported in the literature. The majority of amines detected could be a result of natural sources, but anthropogenic sources could also be a possibility. In water, the finding that DMA and MA were correlated to the TOC content in the lakes indicated that some of these amines could be ascribed to natural sources.

### 7.3.3 A simple and initial environmental risk assessment

A review of the toxicity of selected primary amines and secondary products to aquatic organisms was performed in 2008 (Brooks, S. and Wright, R.F. 2008). Our initial environmental risk assessment is based on this review, and no extensive literature search for more updated PNEC values has been performed since this was not the scope in this baseline study.

In **Table 7.3.1**, the environmental risk assessment for amines, nitrosamines and nitramines are summarised. The numbers for LOEC (lowest observed effect concentration), assessment factor and PNEC value (Predicted No Effect Concentration) were taken from Brooks and Wright (2008). The maximal measured environmental concentration (MEC) in water was taken from **Table 5.3.5** and **Table 5.3.6**. Where the compound was not detected, the LOD was inserted. An environmental risk quotient (MEC/PNEC) is also given, in cases where the LOD has been inserted, this is a maximal estimate. When the risk quotient is lower than 1, this indicates that there is little risk for negative environmental consequences. As can be seen from **Table 7.3.1**, the risk quotient was far below 1 for all the amines assessed, and also for the nitrosamines and nitramines. However, it must be kept in mind that we did not have PNEC values for the amines detected at the highest levels. DMA was detected at a level of  $49 \mu\text{g L}^{-1}$ , which is above the lowest PNEC observed for MDEA ( $5 \mu\text{g L}^{-1}$ ).

**Table 7.3.1** Summary of factors influencing the environmental risk assessment

<i>Compound</i>	<i>LOEC (<math>\text{mg L}^{-1}</math>)</i>	<i>Assessment factor</i>	<i>PNEC (<math>\mu\text{g L}^{-1}</math>)</i>	<i>Max MEC (<math>\mu\text{g L}^{-1}</math>)</i>	<i>MEC/PNEC</i>
MEA	0.75	100	7.5	0.65	0.09
AMP	20	1000	20	0.50	0.025
MDEA	0.5	100	5	n.a.	
PIP	10	100	100	<0.01	<0.0001
Nitrosamines	0.025	1000	0.025	<0.0007 <sup>a</sup>	<0.028
Nitramines	0.2	1000	0.2	<0.0001 <sup>b</sup>	<0.0005

n.a. not analysed

<sup>a</sup> All nitrosamines had LOD  $0.7 \text{ ng L}^{-1}$  except N-nitrosodiethanolamine ( $1.1 \text{ ng L}^{-1}$ ).

<sup>b</sup> All nitramines had LOD  $1 \text{ ng L}^{-1}$  or lower except N-Nitro-methylamine which ( $1.5 \text{ ng L}^{-1}$ ).

The recommended tolerable drinking water concentrations for nitrosamines and nitramines was assessed by Låg et al. (2011), and was set at  $4 \text{ ng L}^{-1}$  for the sum of nitrosamines and nitramines. The recommended tolerable concentration was based on the toxicity of NDMA. Since no nitramines or nitrosamines were detected above the LOD, no single compound was detected above the recommended tolerable drinking water concentration. Three of the lakes investigated in the study are in use as sources for drinking water.

## 7.4 Monitoring programme

The monitoring programme was designed to detect changes in the receptors terrestrial vegetation and soil and surface water. Three possible environmental pollution issues were addressed: eutrophication, acidification and risk of toxic effects of amines, nitrosamines and nitramines (A/N/N).

In particular the programme was designed to detect possible effects on concentrations of A/N/N in drinking water, as this is currently viewed as the greatest potential threat to the environment of operation of TCM with amine technology.

If changes in eutrophication and acidification due to N emissions are to be monitored, then a minimum volume of measurements (both in time and space) must be undertaken, such that the results give clear, statistically-significant answers. The monitoring programme here is designed to register changes in eutrophication and acidification resulting from changes in N deposition, regardless of source of the N. At present most of the N deposition in the Mongstad region comes via long-range transport.

Because very little is known about the natural levels of A/N/N in vegetation, soil and surface waters, and no *in situ* measurements of these compounds have been made in the environment in the vicinity of industrial plants using amine technology to capture CO<sub>2</sub>, the monitoring programme was designed to encompass all eventualities. A flexible programme is called for, in which a large number of samples are collected, processed and stored for chemical analysis in the event that concentrations of A/N/N in analysed samples increase to levels above those measured in the baseline survey.

By far the largest number of samples for A/N/N analyses are proposed collected from surface waters (lakes), as the drinking water standard of 4 ng L<sup>-1</sup> (sum of all nitrosamines and nitramines) is perceived as the most stringent with respect to operation of TCM. Most of the samples are to be processed and stored rather than analysed at once, in order to reduce the costs.

The proposed monitoring programme includes monthly sampling of 4 lakes, 3 lakes exposed to deposition from TCM, and one reference lake. Three is the minimum necessary for statistical analyses. Surface water (or outlet) should be sampled monthly, but only 1 of 4 samples analysed immediately. In addition deep water in the lakes should be sampled twice yearly, in January and July, when the lakes reach maximum thermal stratification. The justification for this is that since nitrosamines are sensitive to light, concentrations may be low in surface water, but high in the dark, deeper water.

We believe that the inclusion of passive sampling of two lakes annually is a valuable monitoring tool. Extensive research has shown that this technique can increase the measuring capability of compounds in low concentrations. A calibration study of nitrosamines in passive sampling has recently been performed (Kaserzon et al. 2011).

The proposed monitoring programme has a level-of-effort approximately the same as the baseline study. Clearly the monitoring programme can be reviewed regularly in the future and reduced in the event that none of the samples reveals significant change relative to baseline. Such a monitoring programme could be quite flexible, and the level of effort made to reflect the actual emission levels from TCM, and the risk of environmental effects of these emissions.

## 8. Conclusions

The emissions to the atmosphere from CO<sub>2</sub> Technology Centre Mongstad contain amines and may in addition contain or lead to the formation of degradation products from amine-based CO<sub>2</sub> capture technology. An environmental baseline survey was conducted in 2011 prior to the operation. The survey describes the environmental situation with respect to eutrophication (N enrichment), acidification and concentrations of amines and degradation products in terrestrial and aquatic ecosystems.

### Terrestrial vegetation

- The *Calluna*-dominated heaths are nitrogen poor and additional nitrogen will speed up the process in which abundance and composition of species move towards a higher dominance of grass species.
- Terrestrial eutrophication indicators are unlikely to respond to an additional nitrogen deposition from TCM of about 0.03 kg N ha<sup>-1</sup> yr<sup>-1</sup> (c. 0.3% increase).
- However, if the worst case scenario applies (0.7 kg N ha<sup>-1</sup> yr<sup>-1</sup>), slow and gradual changes in the heathlands, growth rate of pine and algae on birch stems may occur.

### Aquatic organisms

- Nitrogen emissions from TCM could lead to increased biomass of benthic algae at oligotrophic sites.

### Water chemistry

- The 30 lakes surveyed comprise acid sensitive, eutrophic, and pristine surface waters. Increased deposition of nitrogen can lead to acidification of surface water with low acid neutralising capacity.

### Amines, nitrosamines and nitramines

- Ten water samples and 8 plant and soil samples were analysed for 7 amines, 5 nitramines and 9 nitrosamines. The level of detection for the compounds was in the ng L<sup>-1</sup> and ng g<sup>-1</sup> or lower for all compounds.
- None of the nitramines or nitrosamines was detected above the detection limit in any of the samples investigated.
- All the amines investigated except piperazine (and 2-amino-2-methylpropanol in soil), were detected in all the materials investigated.
- Amine levels ranged from low ng g<sup>-1</sup> to almost µg g<sup>-1</sup> in plant and soil samples, and 10 ng L<sup>-1</sup> to 50 µg L<sup>-1</sup> in water depending on the amine.
- Dimethylamine, a natural constituent of many plants, was found in highest levels in all matrices.
- The levels of dimethylamine and methylamine in water were correlated with the total organic carbon concentration.
- The majority of amines detected can come from natural sources, but anthropogenic sources can also be a possibility.

### Chemical screening

- A broad chemical screening by gas-chromatography time-of-flight mass spectrometry and liquid-chromatography quadrupole mass-spectrometry was performed. The data have been saved for later comparison.

Risk assessment

- A simple and initial environmental risk assessment showed that the levels of most amines, nitrosamines and amines were far below the PNEC values that have been reported; risk assessment for several amines was not feasible, however, since PNEC values have not been assigned for all compounds.

Monitoring programme

- Based on the scientific results in this report, a future monitoring program was proposed.

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## 10. Appendices

### 10.1 Abbreviations

A/N/N	amines, nitrosamines, and nitramines
AIP	acidification index periphyton
Al/II	non-labile aluminium
Al/R	reactive aluminium
Alk	Alkalinity
AMP	2-amino-2-methyl-propanol
BSTFA	N,O-Bis(trimethylsilyl)trifluoroacetamide
Ca	Calcium
CAS	Chemical Abstracts Service
Da	Dalton
Cl	chloride
DBH	diameter at breast height
DCM	Dichloromethane
DEA	diethylamine
DMA	dimethylamine
EPA	Environmental Protection Agency
GC	gas chromatography
K	potassium
LAI	leaf area index
Lal	labile aluminium
LC	liquid chromatography
LOD	limit of detection
LOEC	lowest observed effect concentration
MA	methylamine
MEA	ethanolamine
MEC	Measured environmental concentration
Mg	magnesium
MS	mass spectrometry
N	nitrogen
Na	sodium
NFLI	Norwegian Forest and Landscape Institute
NH <sub>4</sub>	ammonium
NILU	Norwegian Institute for Air Research
NIVA	Norwegian Institute for Water Research
NIST	National Institute of Standards and Technology
NO <sub>3</sub>	nitrate
PIP	piperazine
PIT	periphyton index of trophic status
PNEC	predicted no effect concentration

SO <sub>4</sub>	sulphate
SPE	Solid Phase Extraction
TCM	CO2 Technology Centre Mongstad
TCMS	Methyltrichlorosilane
TOC	total organic carbon
ToF	Time of flight
Tot-N	total nitrogen
Tot-P	total phosphorus

## 10.2 Personnel

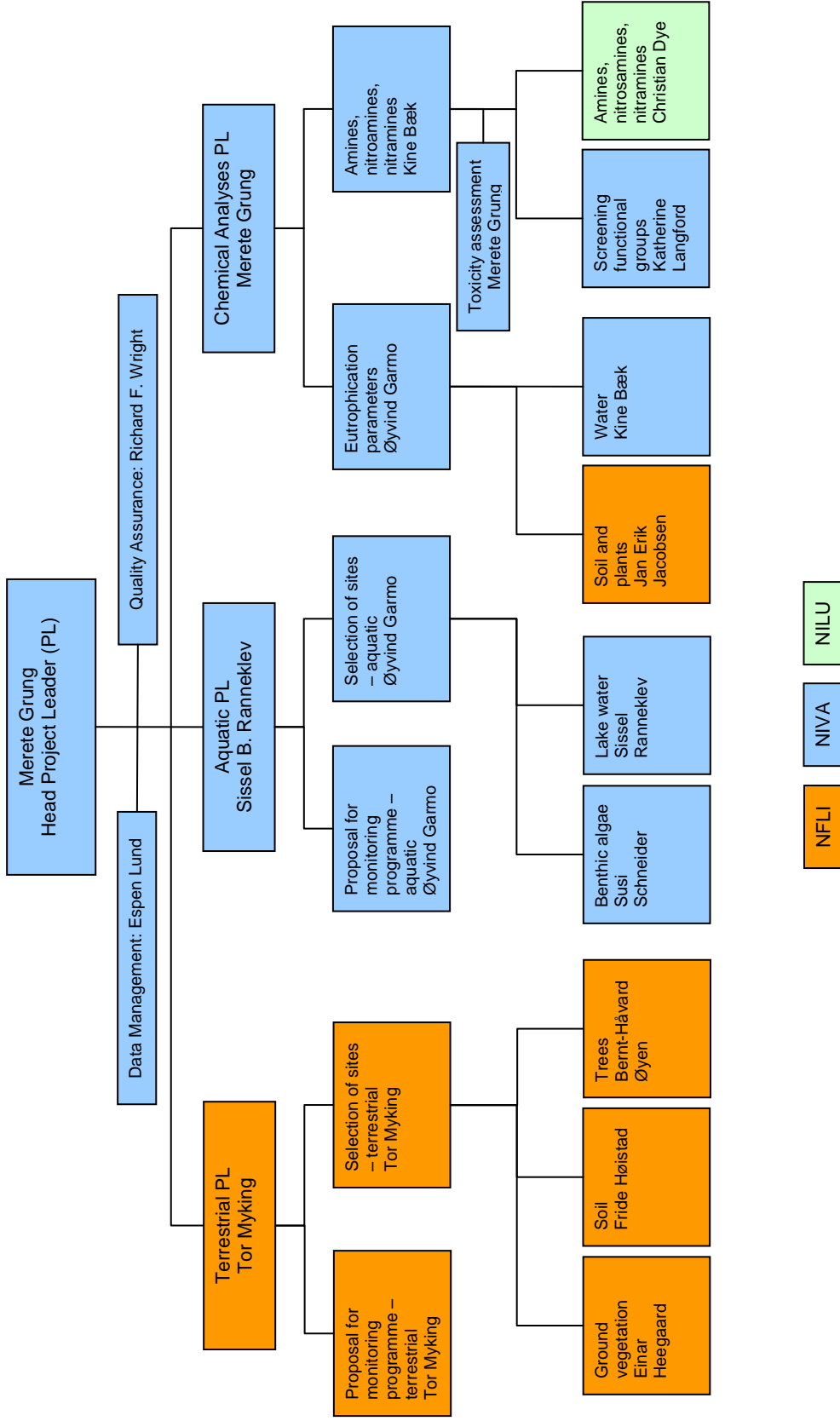
The following people at NIVA participated in the project.

- **Merete Grung**, PhD – environmental toxicologist. Grung is a senior scientist with 20 years' experience with chemistry, environmental chemistry and environmental toxicology. She acted as the project leader.
- **Richard Wright**, PhD – environmental chemist. Wright is a senior research scientist with 35 years of experience in hydrochemical research, including field studies, catchment-scale experiments and modelling. Wright quality assured the project and acted as senior advisor.
- **Sissel Brit Ranneklev**, PhD – environmental chemist. Ranneklev has experience environmental monitoring projects and projects related to the Drinking water Directive. She was responsible for the aquatic sampling and reporting of the aquatic parameters.
- **Øyvind Garmo**, PhD – environmental chemist. Garmo has experience with environmental monitoring and aquatic toxicology. His responsibility was characterisation and reporting of surface water and proposal of aquatic monitoring
- **Susi Schneider**, PhD – limnologist. Schneider has developed the index for benthic ecology, and was responsible for field work, assessment and reporting related to growth of benthic algae.
- **Linda Marie Skryseth**, MSc – ecotoxicologist. Skryseth assisted in the field work related to aquatic sampling.
- **Maia Røst Kile**, MSc – biologist. Kile assisted in the field work relating to benthic algae.
- **Espen Lund**, MSc – ecologist. Lund was responsible for working with chemical, biological and GIS datasets related to the project.
- **Katherine Langford**, PhD – analytical chemist. Langford has experience with method development for the determination of new and emerging contaminants, as well as chemical analysis to support toxicity testing experiments. Her responsibility was chemical screening for compounds.
- **Kine Bæk**, MSc – analytical chemist. Bæk is head of the organic chemistry group with NIVA, and was responsible for collection of chemical data and extraction of samples for storage and screening.
- **Malcolm Reid**, MSc – analytical chemist. Reid assisted with screening for compounds.

The following people at NFLI participated in the project.

- **Tor Myking**, PhD – plant physiologist. Myking is a senior scientist and was project leader on behalf of NFLI. He has experience from a number of terrestrial monitoring projects in Norway and elsewhere.
- **Einar Heegaard**, PhD – vegetation ecologist. Heegaard has broad experience in vegetation analysis from various projects and is a skilled bio-statistician. Heegaard was responsible for the vegetation analysis.
- **Fride Høistad**, PhD – student. Høistad defended her PhD thesis spring 2011 on vegetation ecology and was involved in the vegetation analysis and also responsible for sampling of soil and plant material.
- **Hans Blom**, PhD - botanist. Blom is an expert taxonomist and was involved in the vegetation analyses, particularly identification of mosses and lichens.
- **Hans Nyeggen**, - forest engineer. Nyeggen has long experience in various kinds of field work and undertook the assessments of growth and vitality of the forest sites.

- **Jan-Ole Skage**, advisor – forestry. Skage has experience from various projects related to forestry and undertook the assessments of growth and vitality of the forest sites. In addition Skage was responsible for the LAI assessments.
- **Ove Klakegg**, MSc quaternary geology. Klakegg is a senior engineer (mapping, classification, methodology of soils). In the project he advised and supervised the soil sampling in the field.
- **Bernt-Håvard Øyen**, PhD – forester. Øyen is a researcher with a broad experience in estimation of forest production and was responsible for the forest growth component in the project.
- **Nicholas Clarke**, PhD – chemist. Clarke has long experience with forest ecosystem monitoring and research, and participated in the evaluation of the soil chemistry data.
- **Jan Erik Jacobsen**, BSc, chemistry engineer. Jacobsen was responsible for the chemical lab at NLF and has been in charge of chemical analyses in numerous monitoring and research projects over the years.



Organisational chart of involved personnel with assigned tasks

### 10.3 Timetable

Activities	Feb	Mars	April	May	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb
	2011												
Stations/site selection <b>Milestone: stations selected 14/3</b>	x												
Complete basic survey report <b>Milestone: Report due 21/3</b>		x											
Terrestrial investigation Ground vegetation Trees Sampling (soil/plants) <b>Milestone: Terrestrial field work finished 31/8</b>					x x x	x x x	x x x						
Aquatic investigation Surface water sampling Benthic algae field work <b>Milestone: Aquatic field work finished 30/9</b>							x x	x x					
Chemical analysis Analysis – eutrophication parameters Analysis – amines, nitramines and nitrosamines Analytical screening - functional groups <b>Milestone: Analyses finished 31/11</b>							x x	x x	x x x				
Sampling storage <b>Milestone: All samples stored 15/10</b>							x	x	x				
Data handling <b>Milestone: all data stored 31/12</b>						x	x	x	x	x	x		
Report Terrestrial <b>Milestone: Report due 31/12</b>								x	x	x	x		
Report Aquatic <b>Milestone: Report due 31/12</b>								x	x	x	x		
Report chemical analyses <b>Milestone: Report due 15/1-2012</b>										x	x	x	
Proposal monitoring program <b>Milestone: report due 31/1-2012</b>										x	x	x	
Reporting (final) <b>Milestone: Final report due 15/2-2012</b>											x	x	x

#### **10.4 Benthic algae: Species list and abundances at the sampling sites**

Species list and abundances of benthic algae at the sampling sites in the Mongstad area; abundance of species is given as % cover. Species growing on or amongst others are given as x=rare, xx=common, xxx=abundant. Data for MGU GUD and MGU MAR 1998-2009 are taken from Directorate for Nature Protection (2010) and Directorate for Nature Protection (2011).



	MGU GUID 1998	MGU GUID 2000	MGU GUID 2007	MGU GUID 2009	MGU GUID 2011	MGU MAR 1998	MGU MAR 2000	MGU MAR 2007	MGU MAR 2009	MGU MAR 2011	LDY BOT 2001	LDY BOT 2006	LDY BOT 2008	LDY BOT 2010	LDY BOT 2011
<b>Cyanophyceae</b>															
Aphanocapsa spp.															
Capsosira brebissonii															
Chamaesiphon britannicus															
Chamaesiphon confervicola															
Chamaesiphon minutus															
Clastidium setigerum															
Coleodermium sagarmathae															
Cyanophanon mirabile															
Gaellierinema spp.															
Gloeocapsa sanguinea															
Gloeocapsopsis magna															
Heterolebleinia spp.															
Homoeothrix varians															
Homoeothrix spp.															
Merismopedia spp.															
Phormidium spp.															
Schizothrix spp.															
Soytonema mirabile															
Soytonematopsis sp. (grønt lak)															
Soytonematopsis starmachii															
Soytonematopsis (trichom 3-6µ, tynn)															
Soytonematopsis (trichom 3-6µ, tynn)															
Stigonema hormoides															
Stigonema mamillosum															
Stigonema multiparitum															
Stigonema multiparitum															
Tolypothrix penicillata															
Tolypothrix penicillata (Plectonematatype)															
Uridentifiserte coccale blågrønnalger															
Uridentifiserte trichale blågrønnalger															
<b>Chlorophyceae</b>															
Actinoleanidium cruciferum															
Bhucleeria lectorum															
Bulbochaete spp.															
Chaetophorales 3-5µ gjiffiggrønn															
Closterium spp.															
Coleochaete spp.															
Cosmarium spp.															
Draparnalia glomerata															
Draparnalia glomerata (plumosa type)															
Gongosira fluminea															
Gongosira fluminea															
Hormidium flaccidum															
Hormidium rivulare															
Hyalotheca dissiliens															
Microspora palustris															
Microspora palustris var minor															
Myrionecta a (6-12µ)															
Myrionecta a/b (10-18µ)															
Oedogonium a (6-11µ)															
Oedogonium a/b (19-21µ)															
Oedogonium b (13-18µ)															
Oedogonium c (23-28µ)															
Oedogonium d (29-32µ)															
Oedogonium e (65-43µ)															
Penium spp.															
Spicogrya δ (20-42µ, 1K,L)															
Staurium spp.															
Stigeochlorium spp.															
Tetligia granulata															
Tetraspora gelatinosa															
Zygnema a (16-20µ)															
Zygnema b (22-25µ)															
Zygnema sp. (16-20µ)															
Zygnema sp. (16-20µ)															
<b>Rhodophyceae</b>															
Audouinella hermannii															
Bairdichospermum keratophyllum															
Bairdichospermum helminthosum															
Bairdichospermum turrosum															
Bairdichospermum turrosum															
Lemanea spp.															
<b>Xanthophyceae</b>															
Uridentifiserte Rhodophyceae															
Vaucheria spp.															

	LDY MAR 2001	LDY MAR 2006	LDY MAR 2008	LDY MAR 2010	LDY MAR 2011	LSA RAM 2011	LSA MJØ 2011	LSA ANN 2011	LLI IFO 2011	LLI ISK 2011	LLI DAL 2011
<b>Cyanophyceae</b>											
Aphanocapsa spp.											
Capsosira brevisonii					x						
Chamaesiphon britannicus					<1						
Chamaesiphon confervicola										xx	
Chamaesiphon minutus											
Clastidium setigenum											
Coleodesmium sagarmathae		x									
Cyanophanon mirabile											
Gelifeirrema spp.											
Gloeocapsa sanguinea	xxx										
Gloeocapsopsis magna					<1						
Heleorleberinia spp.	x				x						
Homoeothrix spp.											
Homoeothrix varians											
Merismopedia spp.											
Phormidium spp.											
Schizothrix spp.											
Soytonematoopsis sp. (grønt lek)	xx					x					
Soytonematoopsis starmachii	3				<1						
Soytonematoopsis (rødrom 3-6µ, tynt skjede)											
Stigonema hormoides											
Stigonema mamillosum	7	1			<1	2					
Stigonema multipartitum											
Tolypothrix penicillata											
Tolypothrix penicillata (Plectonematype)											
Uridentifiserte coccale blågrønnalger	xx				<1						
Uridentifiserte trichale blågrønnalger	xx										
<b>Chlorophyceae</b>											
Actinaetium crudiferum											xxx
Briacledia tectorum											
Bulbochaete spp.											
Chaetochorales 3-5µ gliffigrønn											
Claestrum spp.											xx
Coleocleate spp.											
Coscinium spp.											
Draparnalia glomerata											
Draparnalia glomerata (plumosatype)											
Gongosira luminensis											
Hamidium laeodum											
Hamidium lividum											
Hyalothecae distans											
Microspora palustris											
Microspora palustris var minor	xx										
Mougeotia a (6-12µ)	xx										
Mougeotia a/b (10-18µ)	xx										
Mougeotia a (5-11µ)											
Oedogonium a/b (19-21µ)											
Oedogonium b (13-18µ)											
Oedogonium c (23-28µ)											
Oedogonium d (29-32µ)											
Oedogonium e (35-43µ)											
Penium spp.											
Spirogyra a (20-42µ, 1K,L)											
Staurastrum spp.											
Stigeochlorium spp.											
Tetraspora granulata											
Tetraspora gelatinosa											
Tetraspora spp.											
Zygnema a (16-20µ)											
Zygnema b (22-25µ)											
Zygnonium sp.3 (16-20µ)	80	15	10		<1						
<b>Rhodophyceae</b>											
Audouinella hermarii											
Batrachospermum keratophyllum											
Batrachospermum helminthosum											
Batrachospermum turfosum											
Batrachospermum turfosum											
Lemanea spp.											
Uridentifiserte Rhodophyceer						xx			xx		
Vaucheria spp.											1

**10.5 Filtration volume of stored samples**

<i>Code</i>	<i>Lab code 11-2168-</i>	<i>Litres extracted</i>
M01	10	2.15
M02	2	1.8
M03	13	2.5
M05	34	2.5
M06	35	2
M08	4	2.2
M09	11	2.5
M10B	16	2.5
M11	9	2.5
M12	17	2.4
M13	27	2.1
M14	24	2.5
M16	18	2.5
M17	14	2.5
M18	5	2.5
M19	12	2.5
M20	6	2.5
M21	19	2.3
M24	28	2.5
M26	3	2.4
M28	33	2.5
M29	25	2.5
M31	26	2.5
M32	8	2.5
M33B	1	2.4
M50	30	2.5
M51	7	2.5
M52	29	2.4
M53	21	2.5
M54	15	2.5

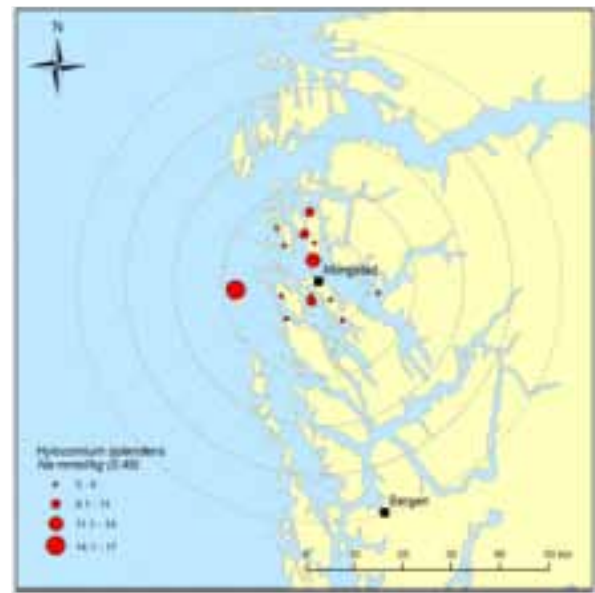
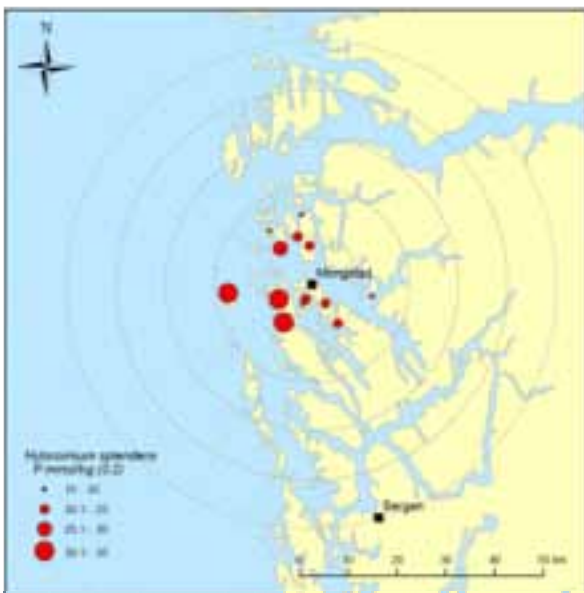
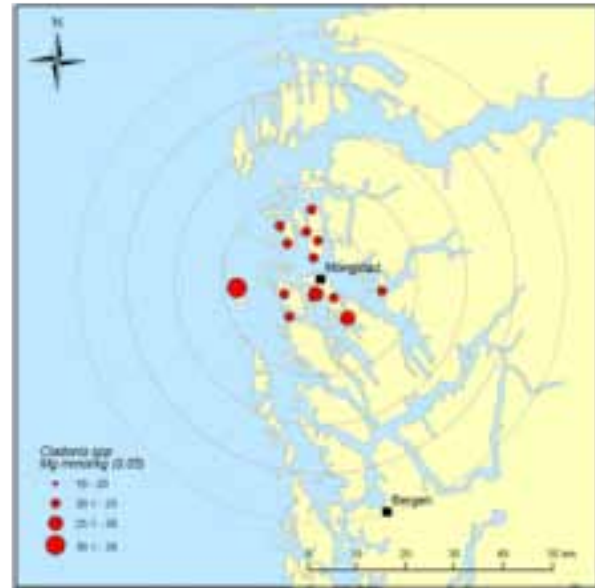
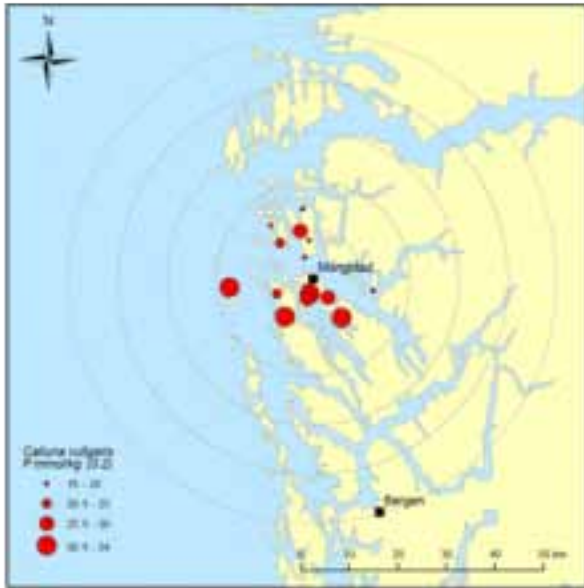
## 10.6 Correlation coefficient matrix

Pearson correlation coefficient matrix ( $\rho$ ) for the 84 quadrants; geographical position east-west and north-south; Ellenberg values light, moisture, pH and nitrogen; and Trich = total number of species, Vrich = number of vascular plant species, Mrich = number of moss species, Lrich = number of lichen species and Crich = number of cryptogam species (mosses and lichens).  $\rho$  values significant at the  $p < 0.01$  level are in bold.

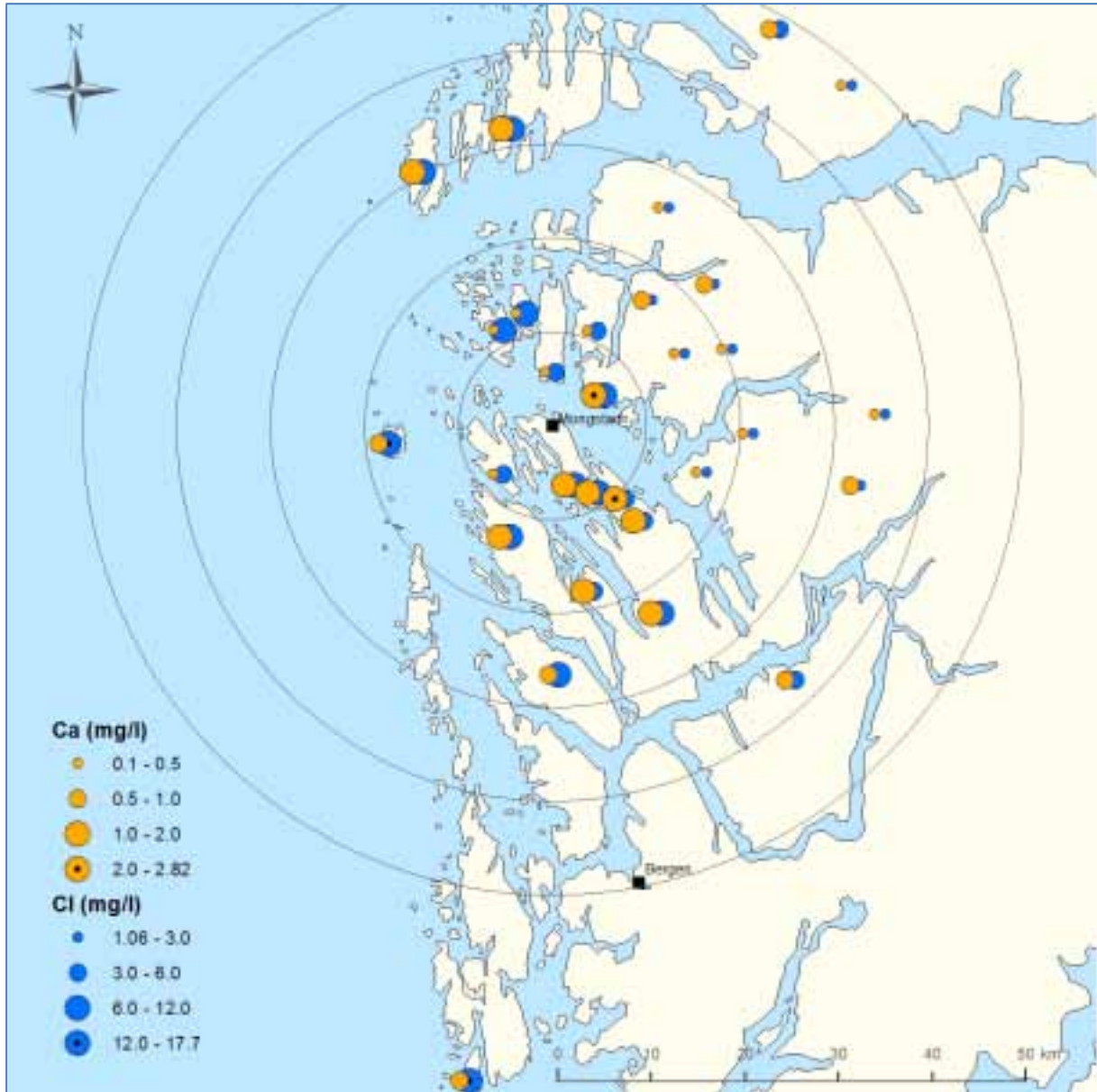
	<i>UTMEW</i>	<i>UTMNO</i>	<i>light</i>	<i>moisture</i>	<i>pH</i>	<i>nitrogen</i>	<i>Trich</i>	<i>Vrich</i>	<i>Mrich</i>	<i>Lrich</i>	<i>Crich</i>
UTMEW	1										
UTMNO	-0.19	1									
light	0.08	0.31	1								
moisture	0.00	0.19	<b>0.78</b>	1							
pH	-0.32	-0.13	-0.01	0.13	1						
nitrogen	-0.22	-0.24	<b>-0.79</b>	<b>-0.61</b>	<b>0.42</b>	1					
Trich	-0.13	-0.12	-0.2	0.04	<b>0.40</b>	0.28	1				
Vrich	-0.22	-0.02	0.15	0.32	<b>0.56</b>	0.20	<b>0.72</b>	1			
Mrich	0.02	-0.17	<b>-0.37</b>	-0.06	0.19	0.20	<b>0.76</b>	0.21	1		
Lrich	0.02	-0.04	-0.28	<b>-0.42</b>	-0.25	0.09	0.31	-0.19	0.20	1	
Crich	0.03	-0.16	<b>-0.42</b>	-0.24	0.03	0.20	<b>0.75</b>	0.08	<b>0.89</b>	<b>0.63</b>	1

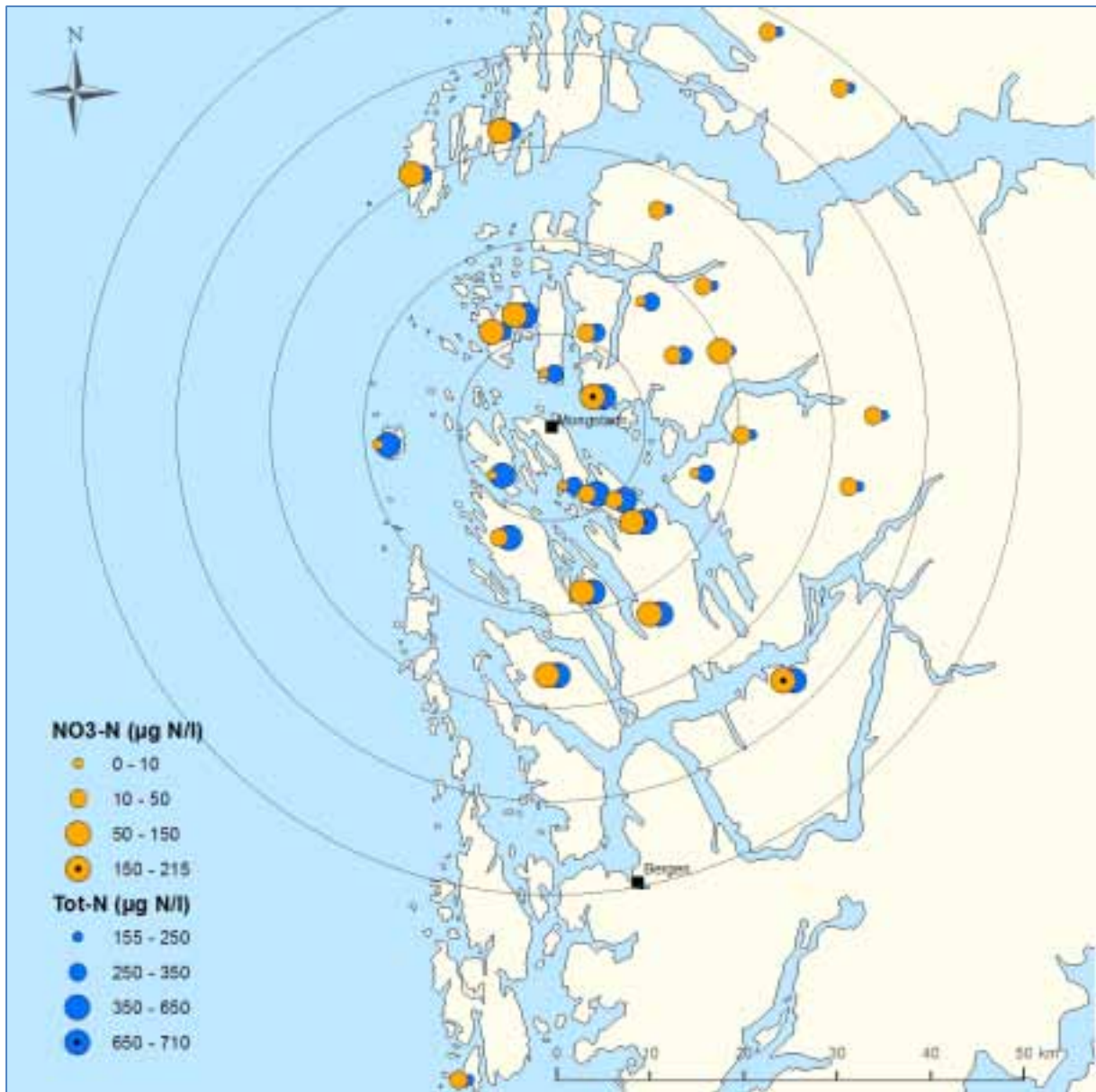


**10.8 Concentrations of some elements in *Calluna vulgaris*, *Cladonia spp*, and *Hylocomium splendens*.**

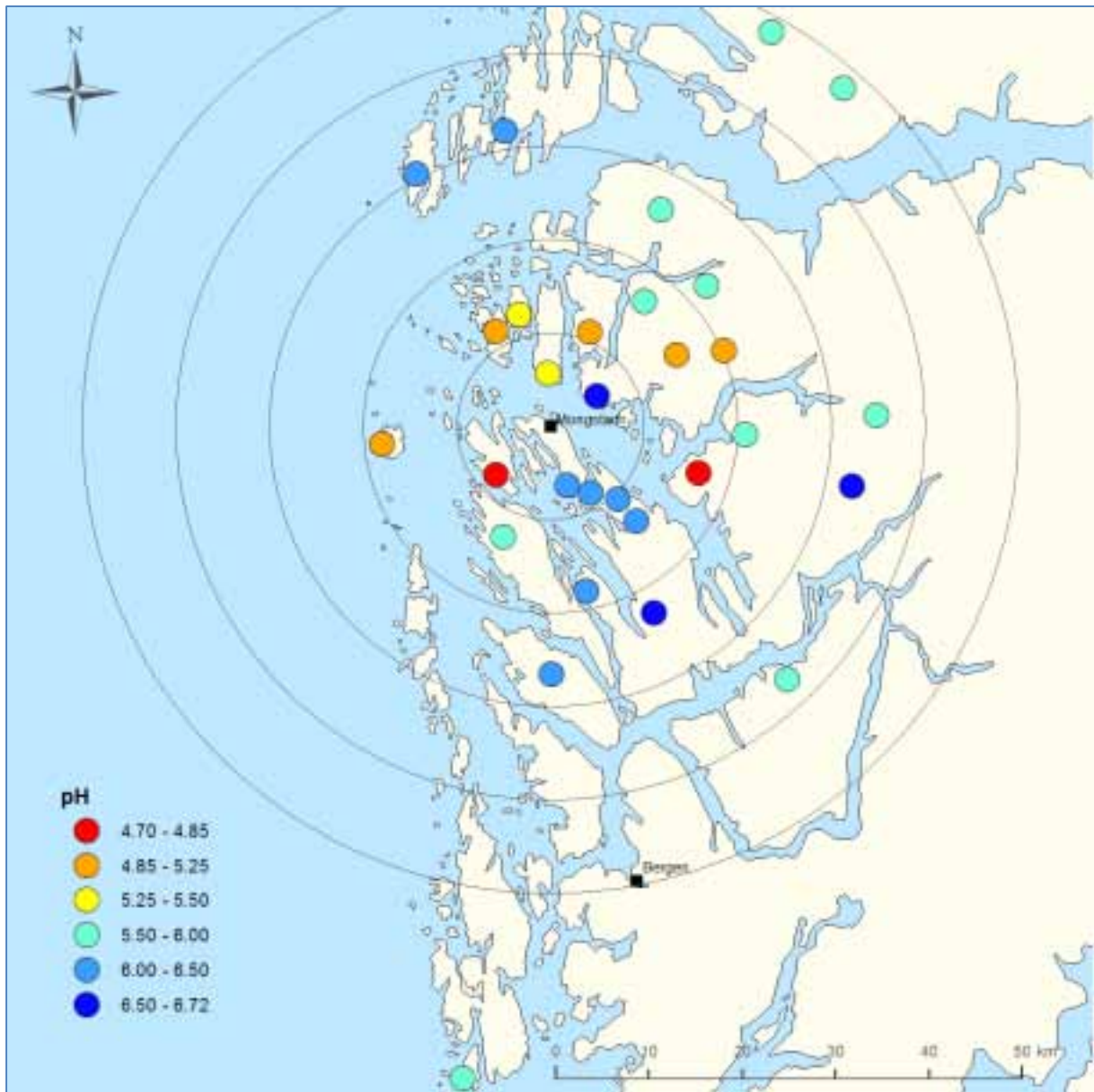


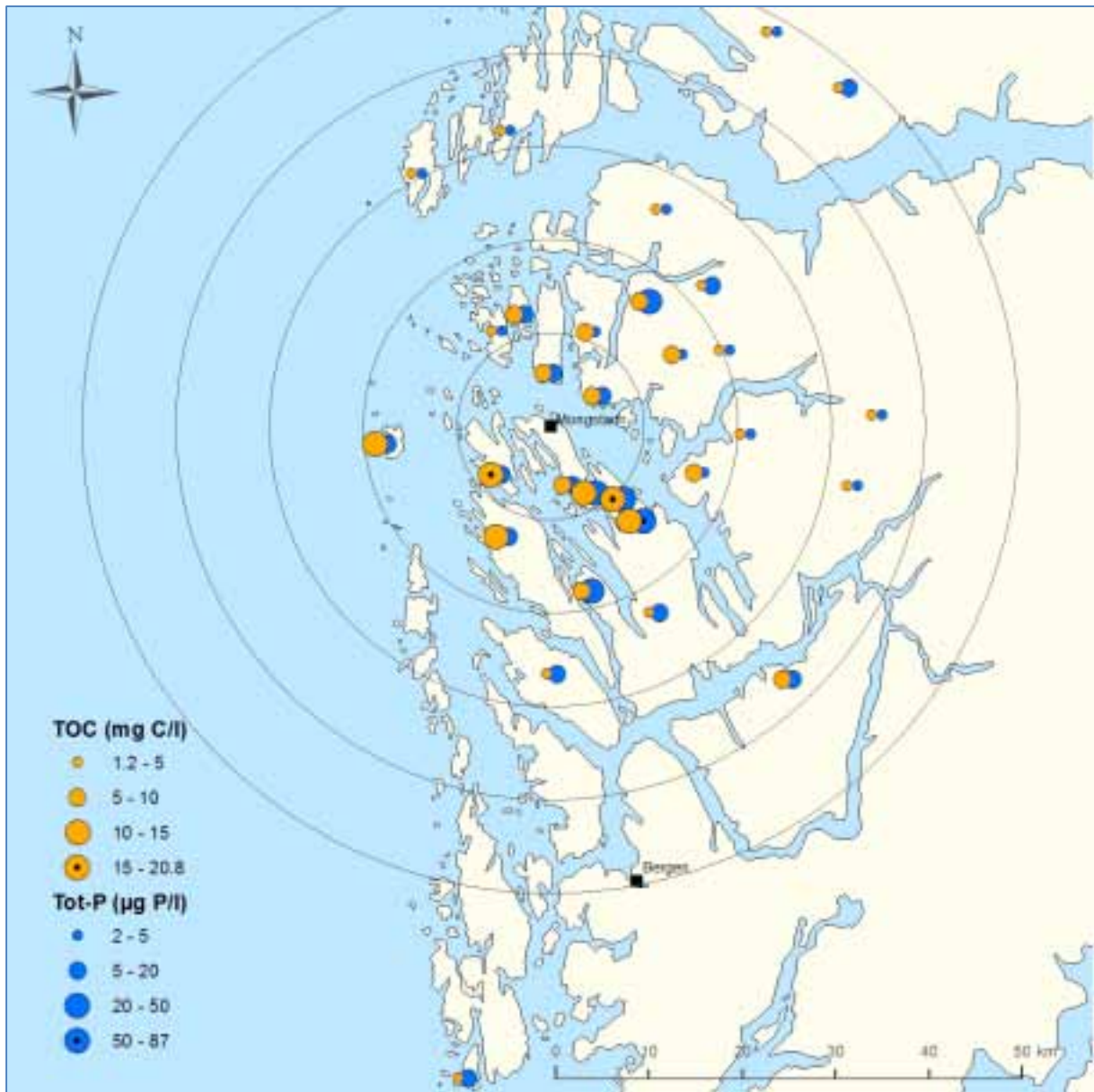
### 10.9 Maps of concentrations of eutrophication and acidification parameters in lake water



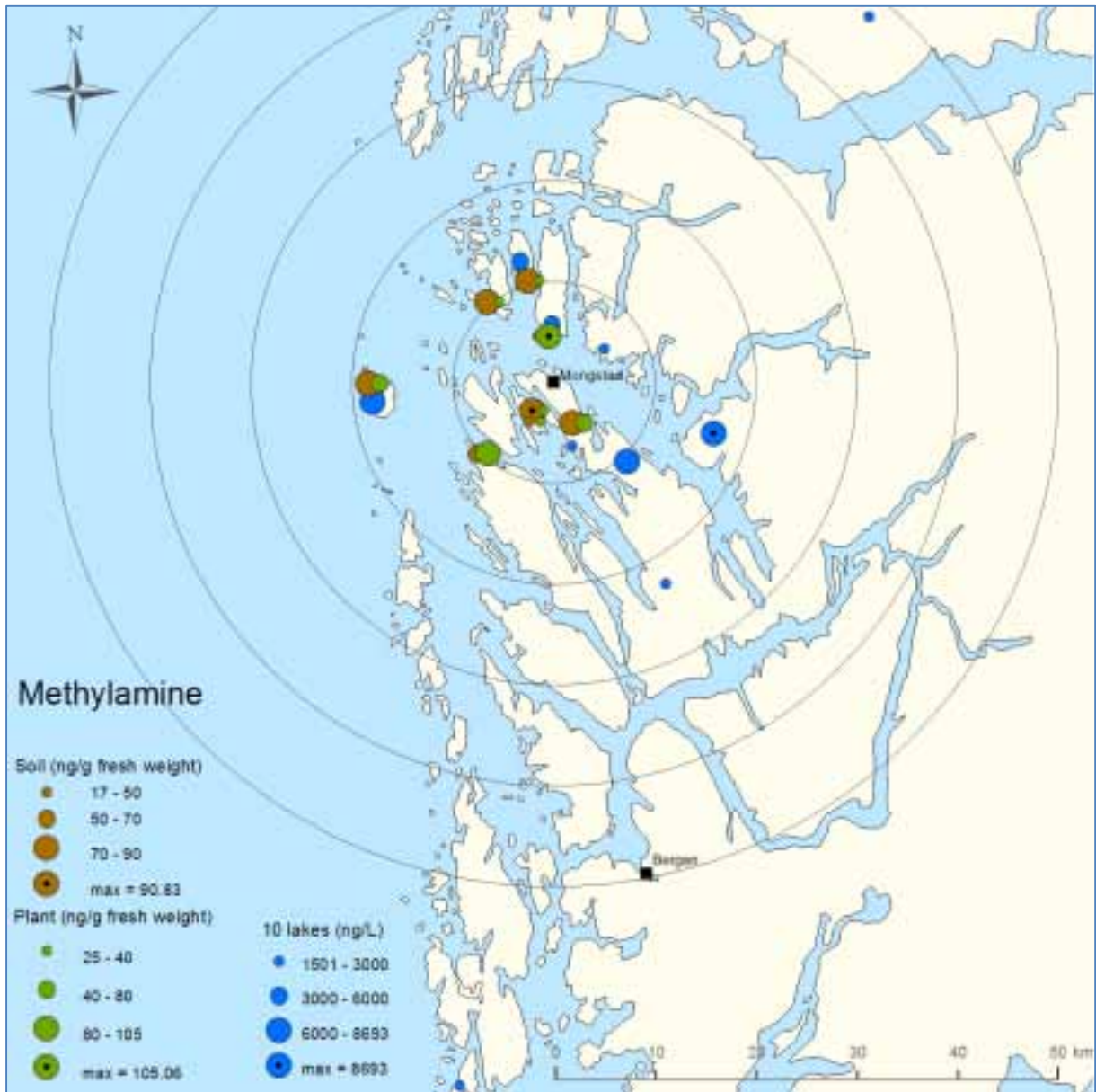


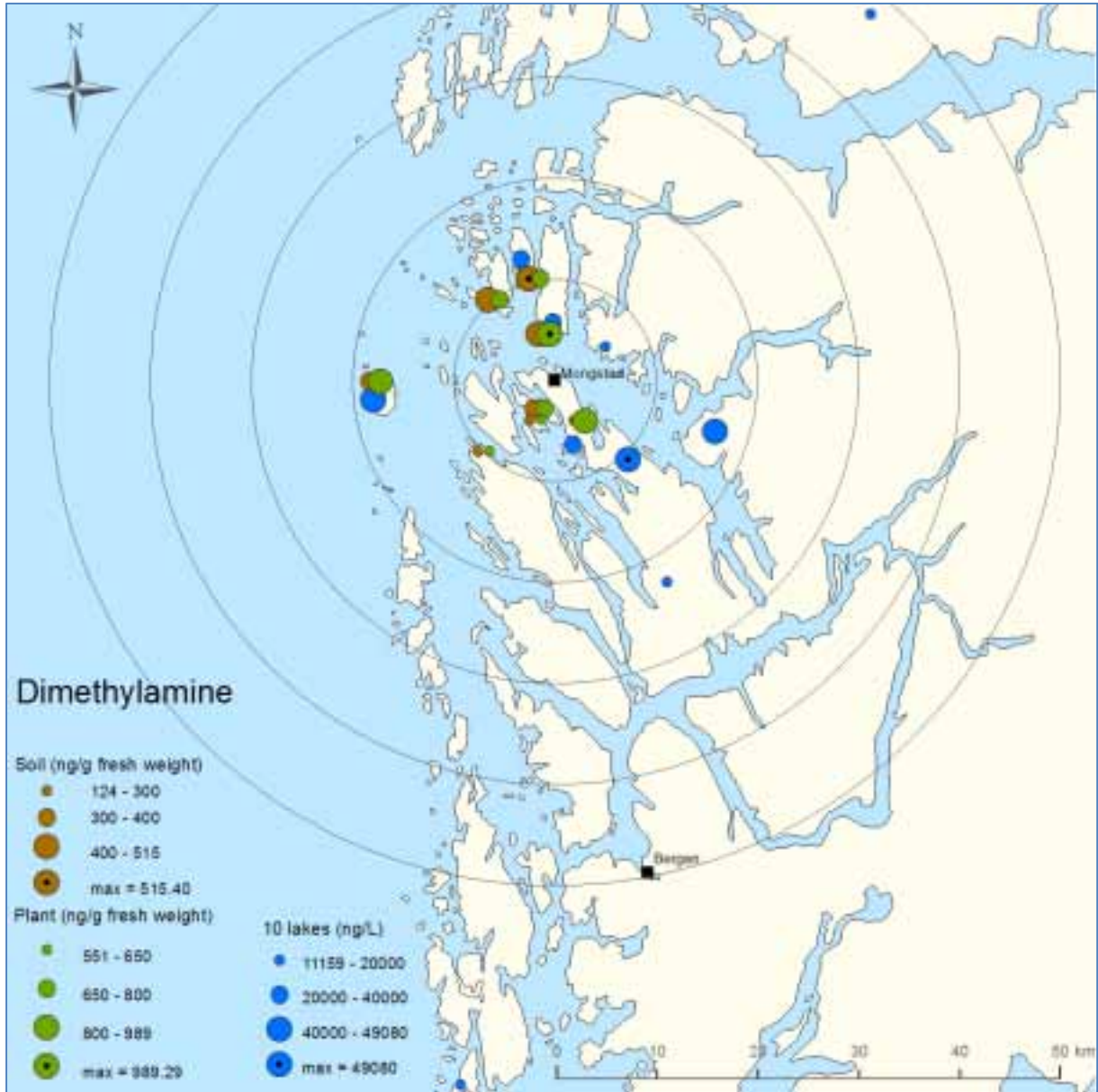




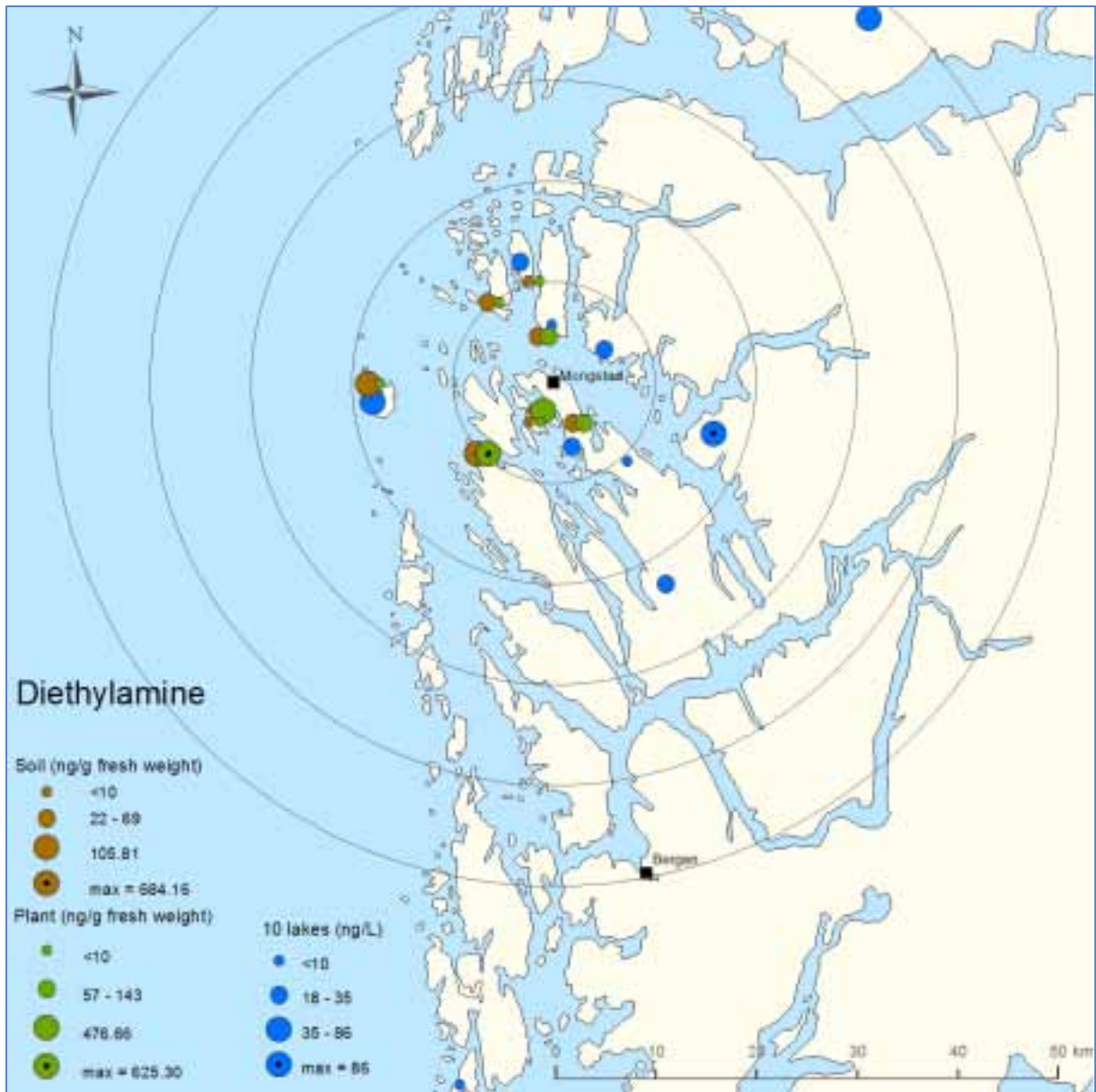


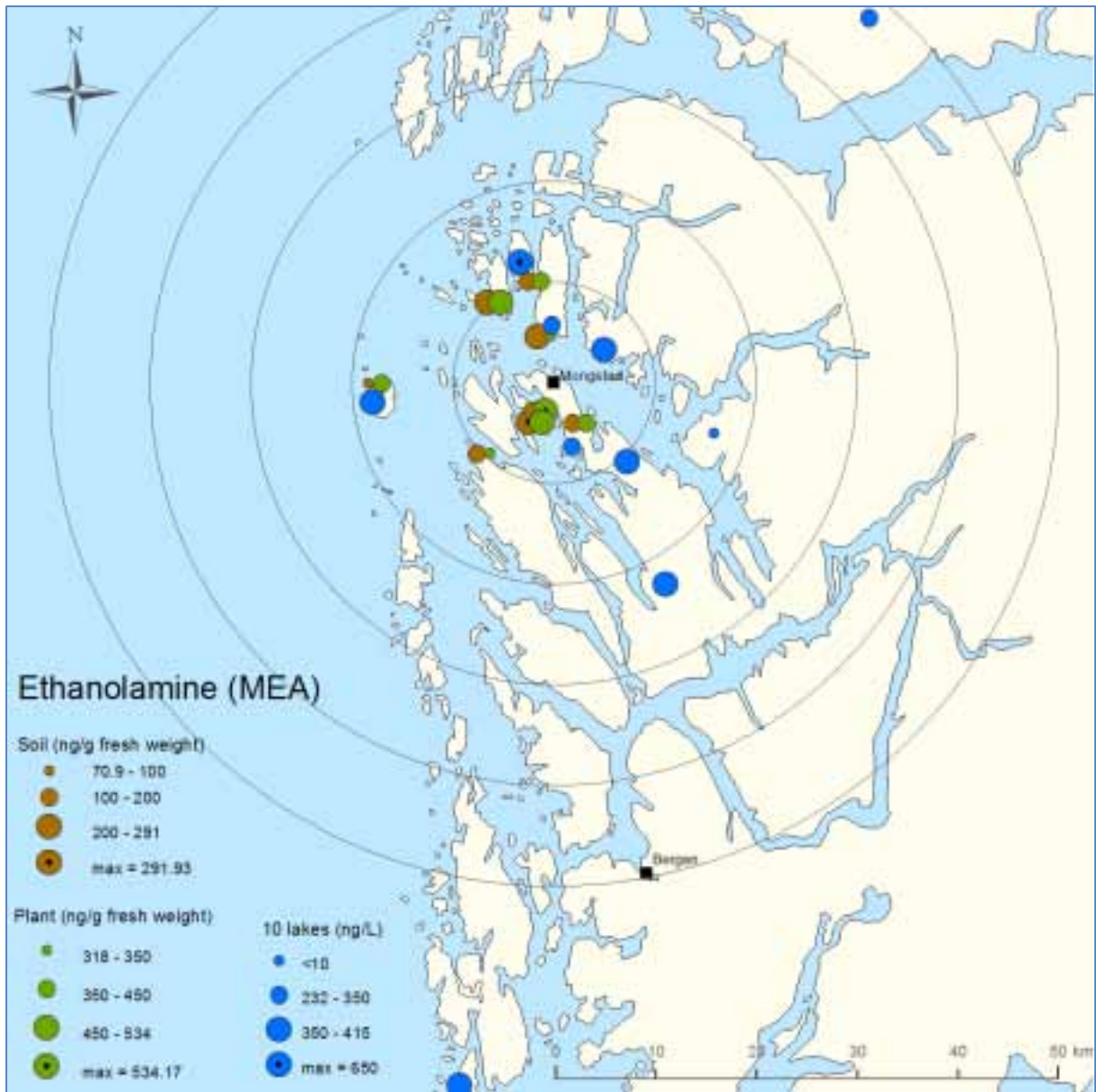
### 10.10 Maps of concentrations of amines in soils, plants and lakes

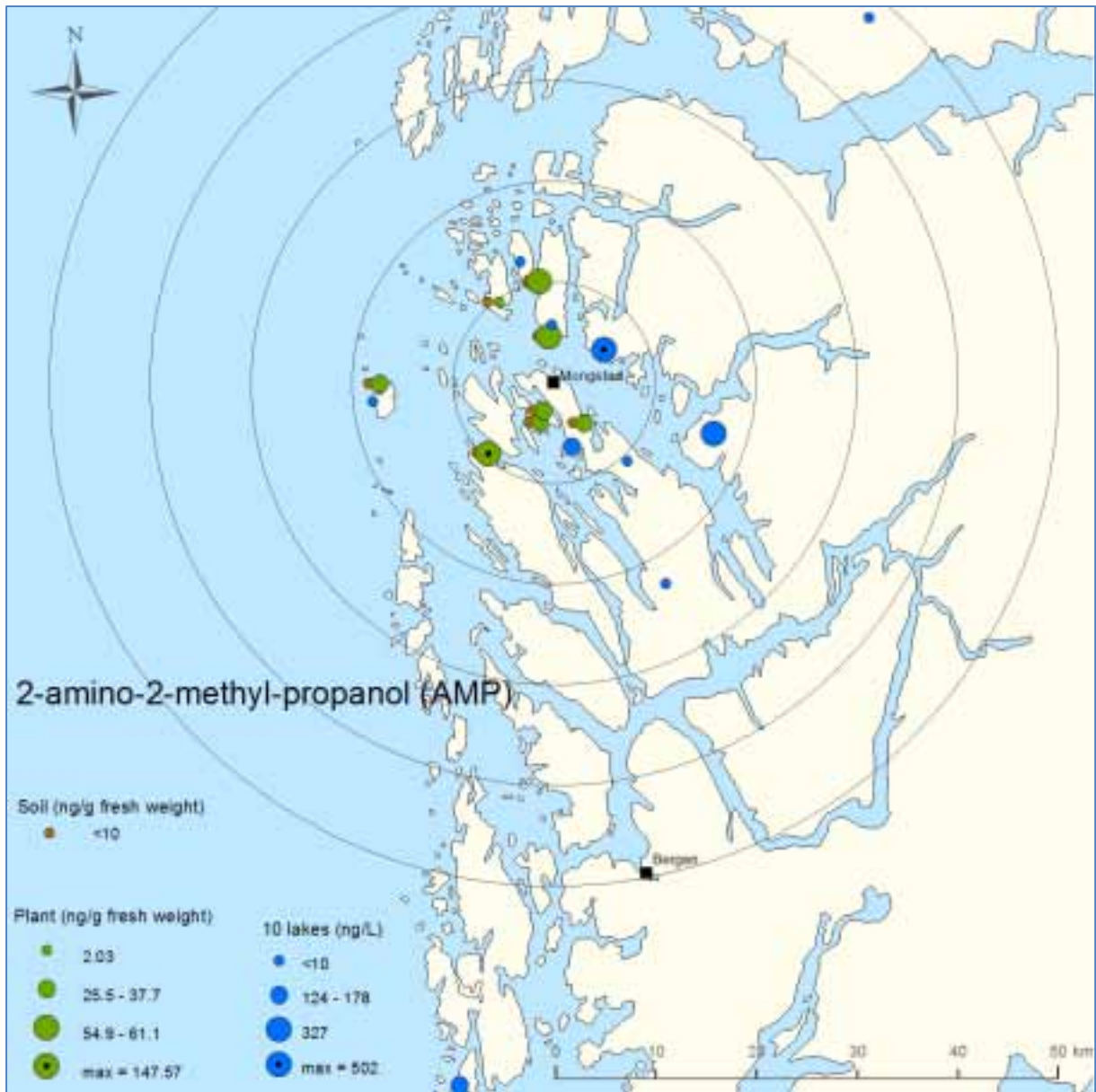




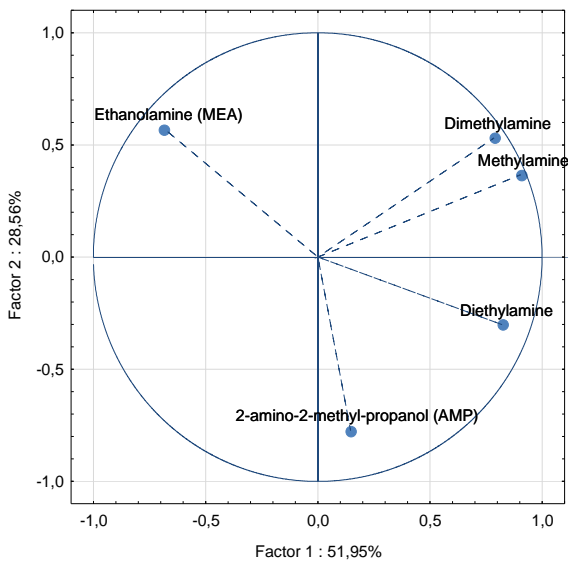
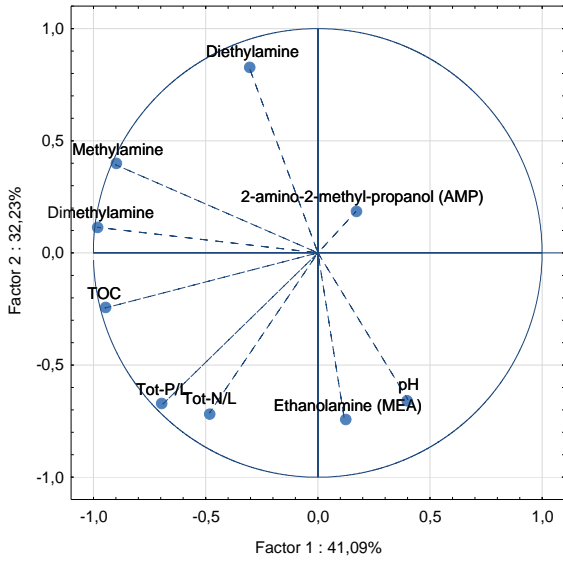
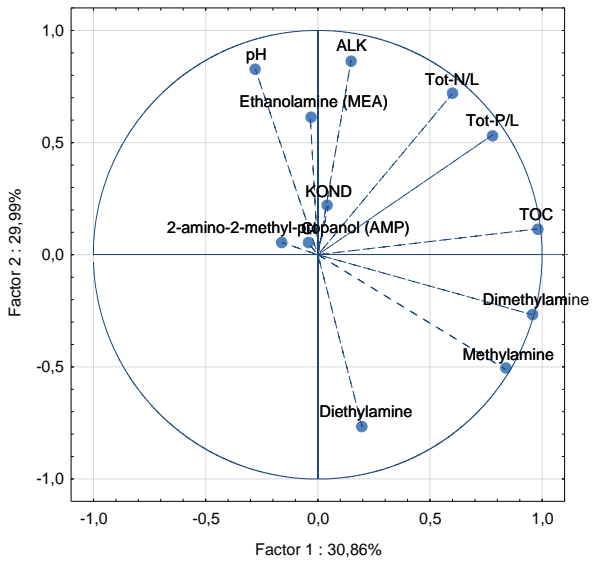








### 10.11 PCA plots of lake water chemistry



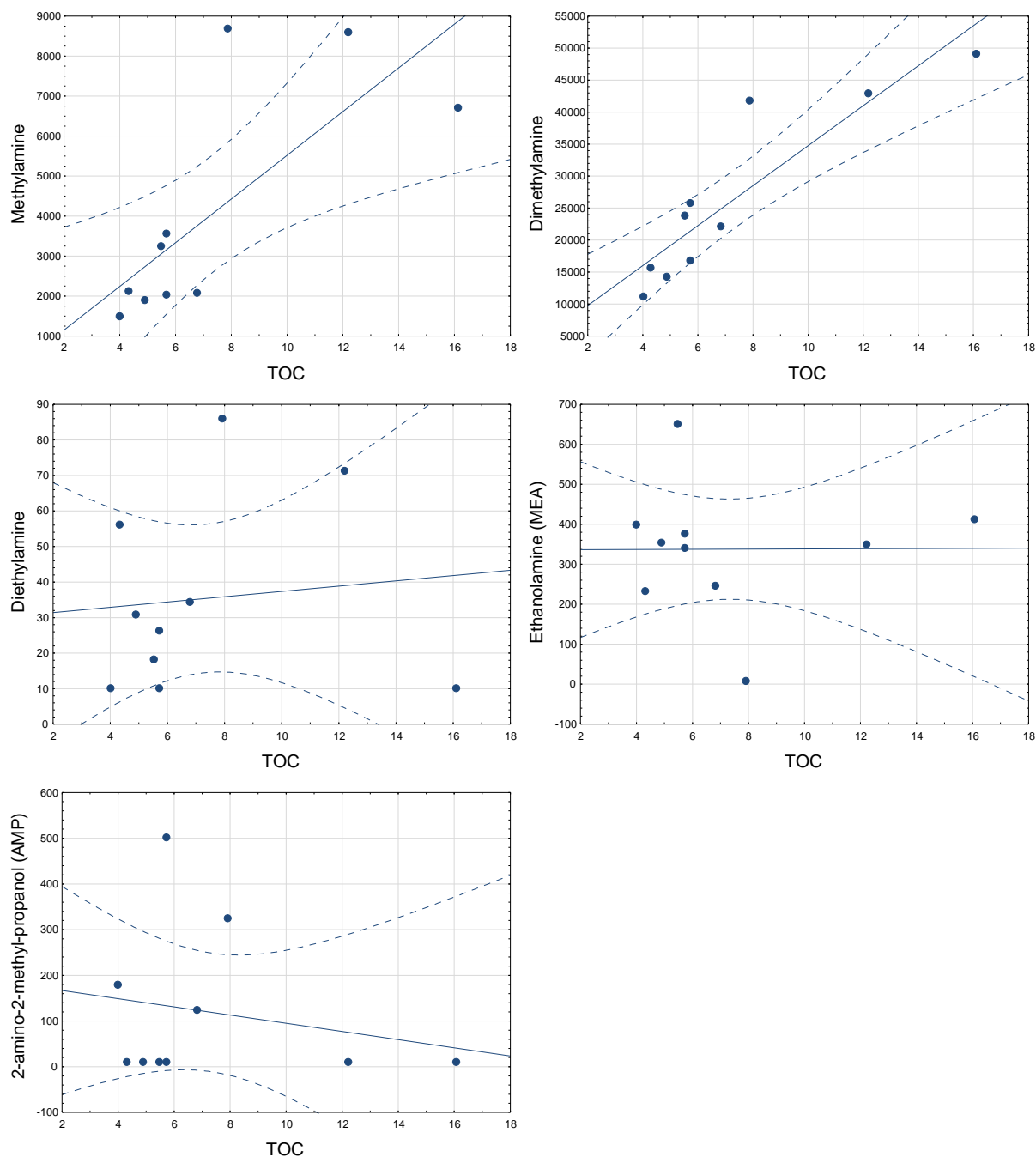


## 10.12 Scatterplot of amines against water chemistry data

All the scatter plots in this section have a regression band and a confidence interval of 95 %.

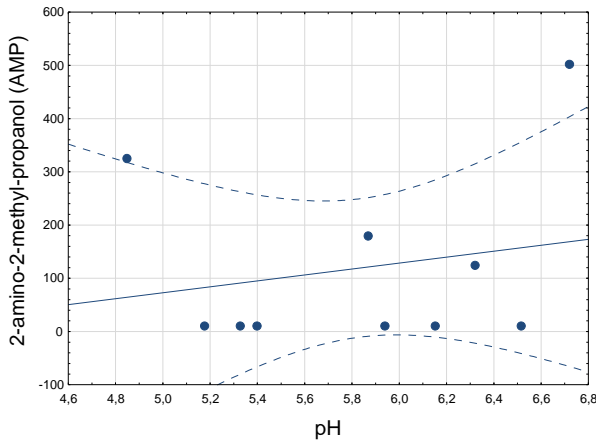
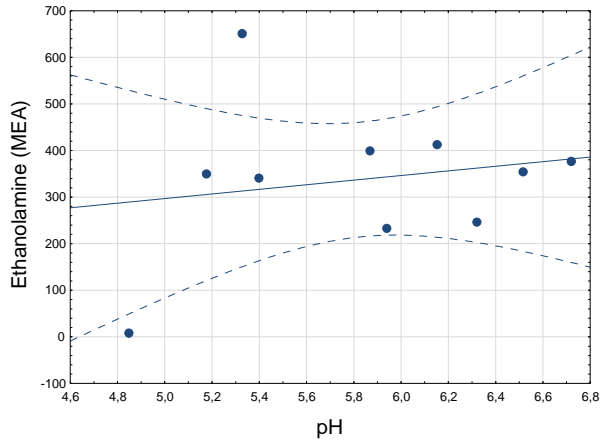
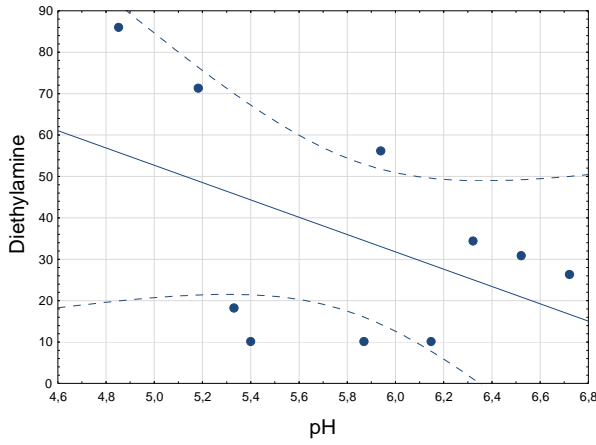
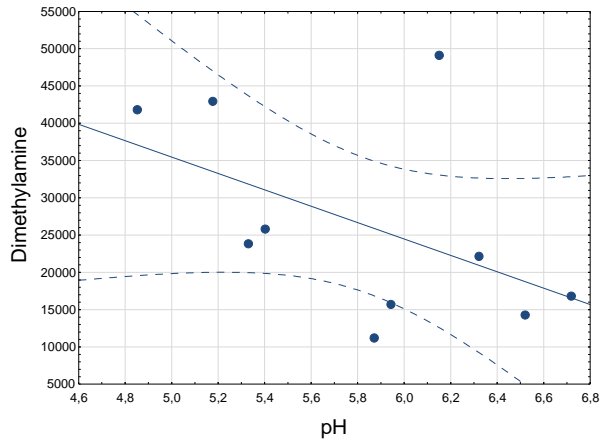
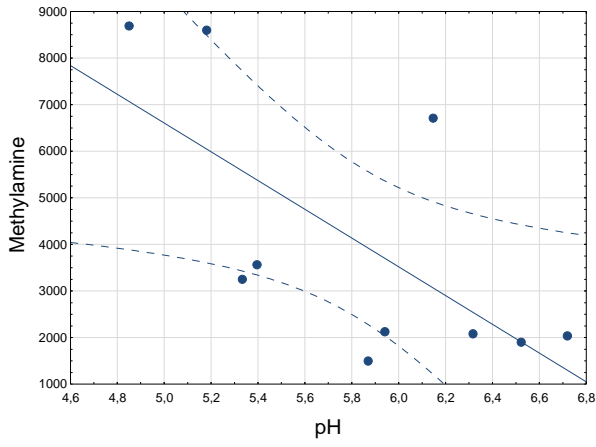
### 10.12.1 TOC

Units: amines ng L<sup>-1</sup>; TOC mgC L<sup>-1</sup>



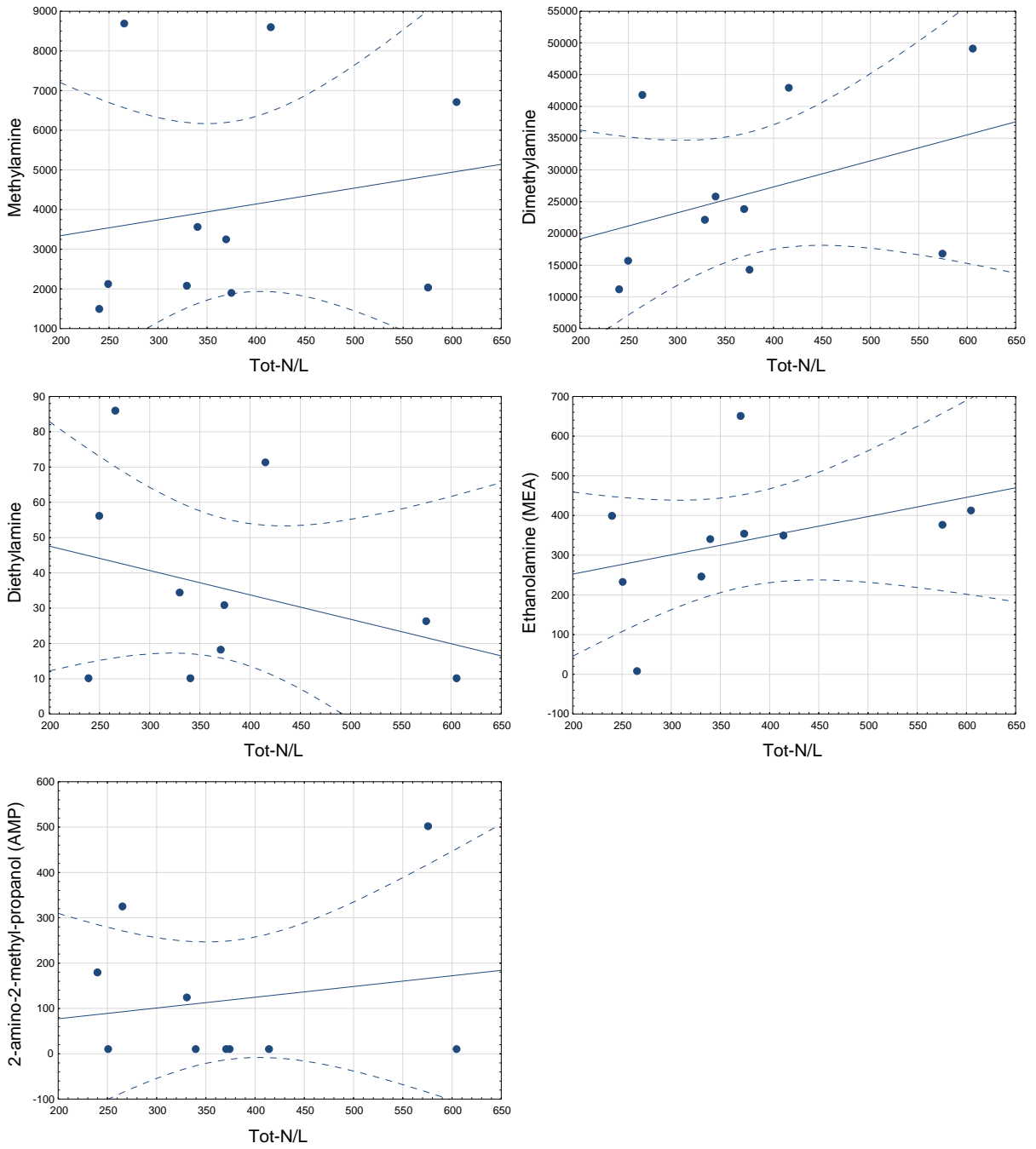
10.12.2 pH

Units: amines ng L<sup>-1</sup>



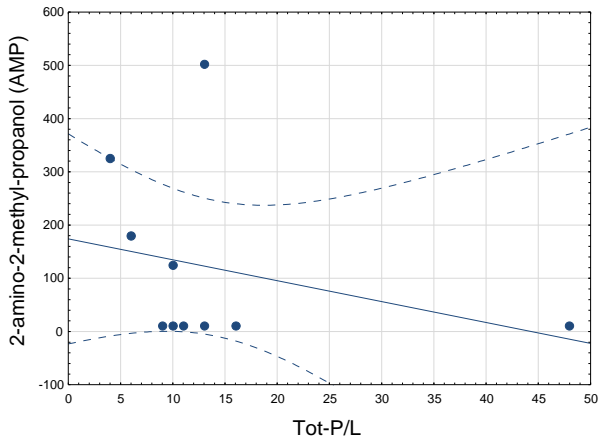
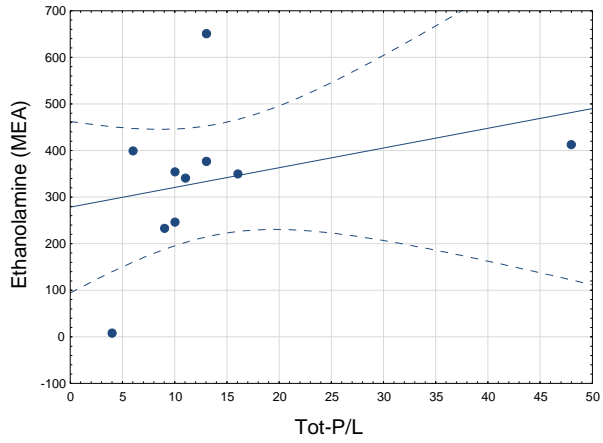
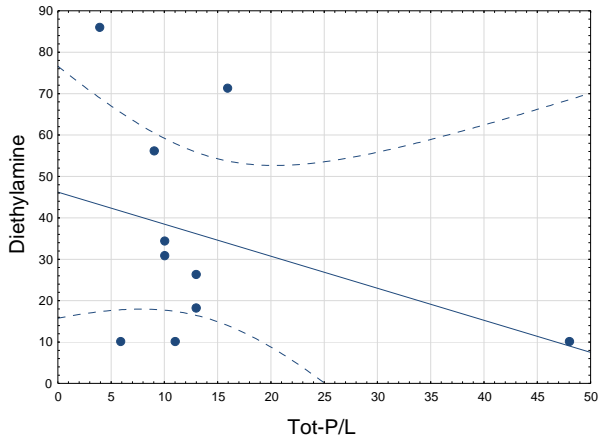
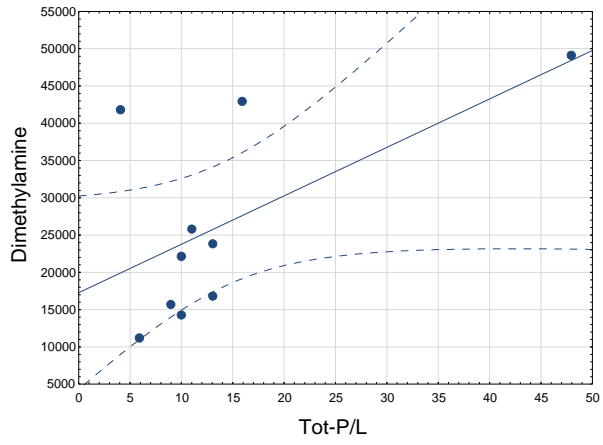
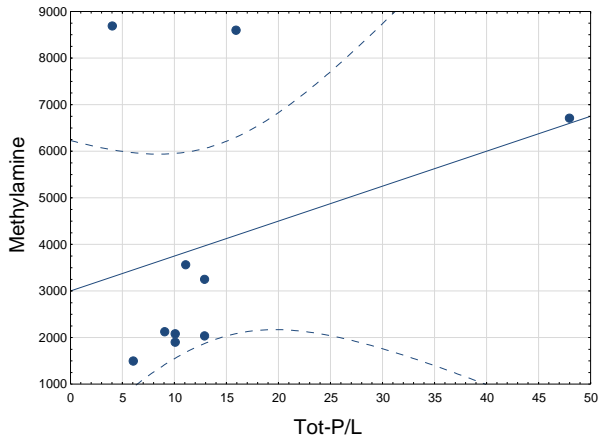
10.12.3 Tot-N

Units: amines ng L<sup>-1</sup>; Tot-N µgN L<sup>-1</sup>



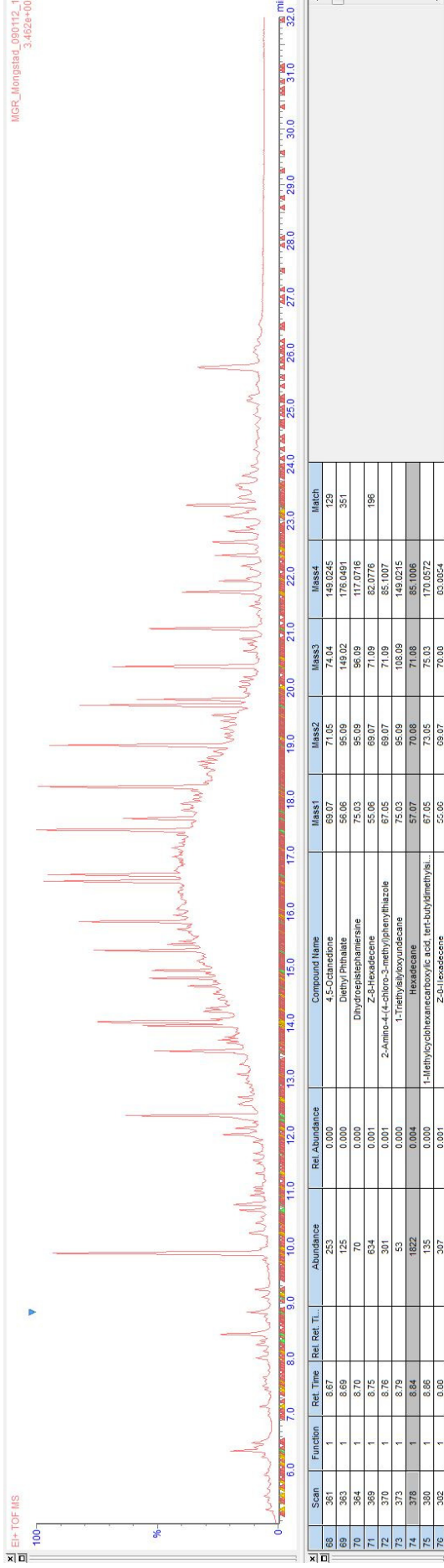
10.12.4 Tot-P

Units: amines ng L<sup>-1</sup>; Tot-P µg L<sup>-1</sup>

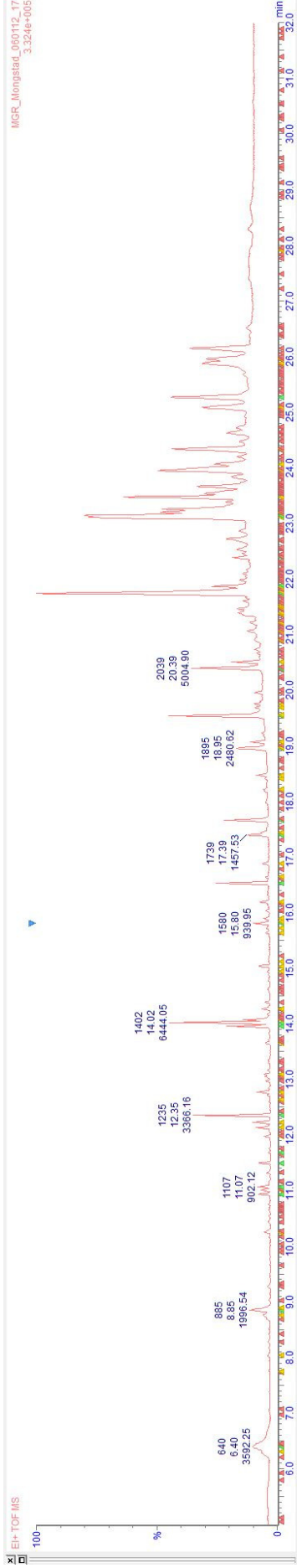




Moss (from G2)– derivatised



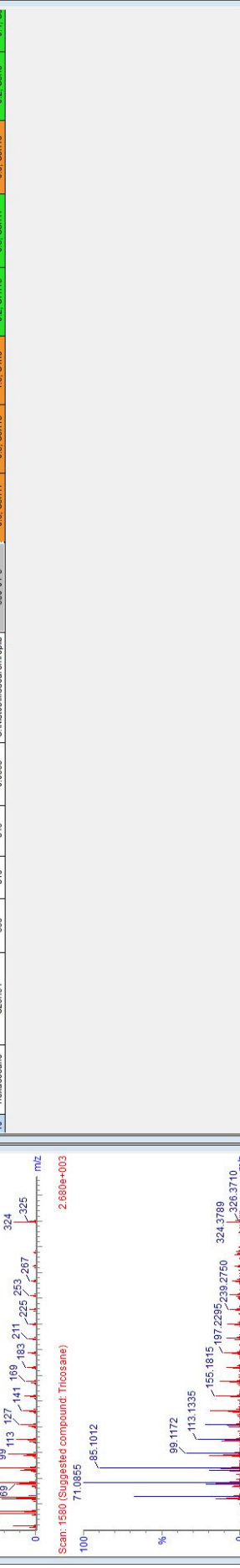
Soil (from G3) – underivatized



Scan	Function	Ret. Time	Rel. Ret. TL	Abundance	Rel. Abundance	Compound Name	Mass1	Mass2	Mass3	Mass4	Match
97	1580	1	15.80	940	0.004	Tricosane	57.07	68.07	71.09	83.0857	
98	1583	1	15.83	46	0.000	7-(1,1-dimethylpropoxy)-4-methoxyfuro[2,3-b]quinoline	97.55	226.14	250.16	251.1671	
99	1589	1	15.89	236	0.001	2-Phenanthrene, 4,5,6,7,8,9,10-octahydro-4b,8,8a-tri-	159.08	175.11	189.13	201.1261	
100	1603	1	16.03	52	0.000	Hexyl 18-methylnonadecanoate	74.04	81.07	83.09	87.0440	363
101	1605	1	16.05	46	0.000	Cyclohexane, 1,1-dicyclohexylmethyl-	81.07	83.08	86.09	87.0899	
102	1614	1	16.14	53	0.000	4-Chloro-5-(1-(2-methoxyphenyl)aminoethyl)benzoic acid	81.07	71.05	81.07	83.0387	520
103	1615	1	16.15	50	0.000	4-Chloro-5-(1-(2-methoxyphenyl)aminoethyl)benzoic acid	71.04	81.07	82.08	83.0384	
104	1618	1	16.19	509	0.002	4,8,12,16-Tetramethylheptadecan-4-olide	69.07	70.08	71.08	83.0859	
105	1632	1	16.32	134	0.001	9-Dodecenoic acid, (Z)-	59.04	72.04	73.05	81.0763	

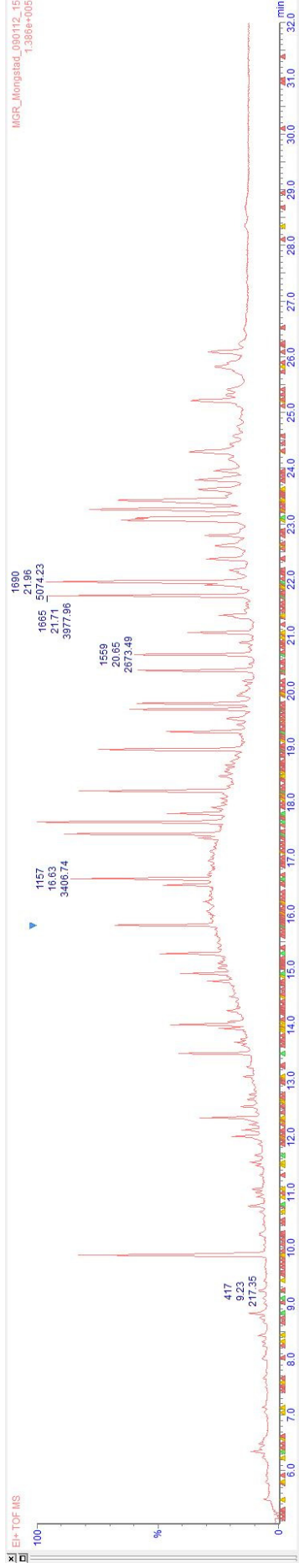
Library Match

Library Name	Formula	Mol. Wt.	Forwar.	Reverse FI	HI Prob	Cas No.	Library Name	Formula	Mol. Wt.	Forwar.	Reverse FI	HI Prob	Cas No.
Tricosane	C23H48	324	885	909	0.4128	71.0855 (mDa)	C:\MSDCHEM\Library	C23H48	324	885	909	0.4128	71.0855 (mDa)
Tricosane	C23H48	324	845	881	0.0557	-0.6 C9H17	C:\MSDCHEM\Library	C23H48	324	845	881	0.0557	-0.6 C9H17
Tricosane	C23H48	324	836	870	0.4128	-0.6 C9H17	C:\MSDCHEM\Library	C23H48	324	836	870	0.4128	-0.6 C9H17
Tricosane	C23H48	324	831	873	0.0559	-0.6 C9H17	C:\MSDCHEM\Library	C23H48	324	831	873	0.0559	-0.6 C9H17
Tricosane	C23H48	324	831	866	0.0559	-0.6 C9H17	C:\MSDCHEM\Library	C23H48	324	831	866	0.0559	-0.6 C9H17
Tricosane	C23H48	324	824	863	0.4128	-0.6 C9H17	C:\MSDCHEM\Library	C23H48	324	824	863	0.4128	-0.6 C9H17
Tricosane	C23H48	324	824	868	0.4128	-0.6 C9H17	C:\MSDCHEM\Library	C23H48	324	824	868	0.4128	-0.6 C9H17
Tricosane	C23H48	324	824	851	0.0447	-0.6 C9H17	C:\MSDCHEM\Library	C23H48	324	824	851	0.0447	-0.6 C9H17
Tricosane	C23H48	324	820	860	0.0378	-0.6 C9H17	C:\MSDCHEM\Library	C23H48	324	820	860	0.0378	-0.6 C9H17
Tricosane	C23H48	324	819	848	0.0363	-0.6 C9H17	C:\MSDCHEM\Library	C23H48	324	819	848	0.0363	-0.6 C9H17





Soil (from G3) – derivatised



Scan	Function	Ret. Time	Rel. Ret. TL	Abundance	Rel. Abundance	Compound Name	Mass1	Mass2	Mass3	Mass4	Match
129	1070	15.76		40	0.000	Stigmatan-7-one	123.12	217.19	232.22	245.2284	
130	1073	15.79		2409	0.017	Tricosane	57.07	71.09	85.10	98.1177	8
131	1075	15.81		518	0.004	1,3,2-Dioxabornane, 2,4-dethyl-5-methyl-5-propyl-	70.08	83.09	84.09	111.1500	
132	1080	15.86		94	0.001	Fluridone	111.12	121.10	133.21	314.2975	38
133	1082	15.88		62	0.000	17,3,6-epoxyprogesterone	111.12	126.08	167.18	169.1663	69
134	1084	15.90		67	0.000	2,1,6-Triethylpyrrolan	85.03	106.03	111.12	169.2012	97
135	1086	15.92		80	0.001	Cholesta-26-ene-3 $\alpha$ ,17,12-trimethoxy-, (3 $\alpha$ ,5 $\alpha$ ,7 $\alpha$ ,12 $\beta$ )-	111.12	113.13	125.13	231.1231	
136	1089	15.95		83	0.001	3,9-Epoxyprogesterone-11,14,16-trimethyl-, (6 $\alpha$ -cyano-3 $\alpha$ ,11 $\alpha$ )-	55.06	121.10	123.12	149.1344	
137	1093	15.99		150	0.001	6-Hydroxy-5-methyl-2,4,10,13,14-pyrimidinone trifins	73.06	247.15	261.17	273.1696	

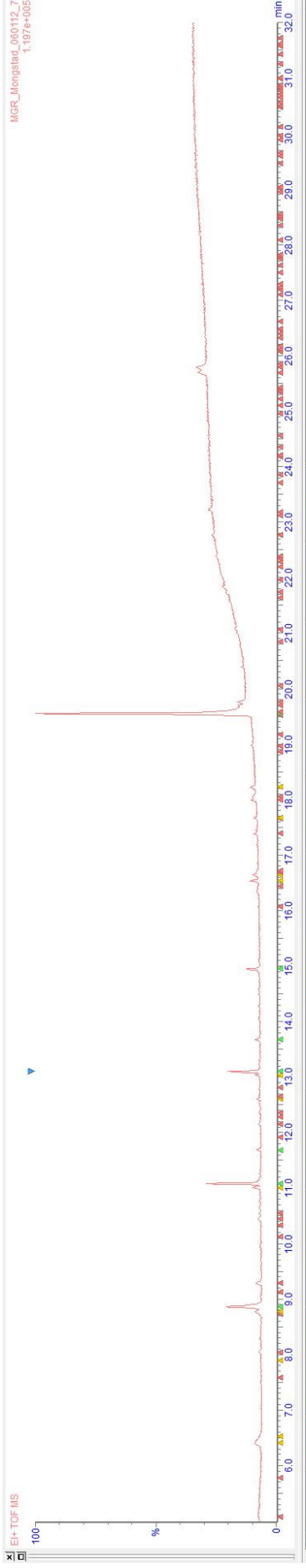
Library Match

Compound	Formula	Mol. Wt.	Forwvar.	Reverse Fit	Hit Prob	Library Name	Cas No.	71.0851 (mDa)	85.1008 (mDa)	57.0716 (mDa)	98.1177 (mDa)	113.1339 (mDa)	127.1495 (mDa)	141.1655 (mDa)	324.3776 (mDa)
1	Tricosane	C23H48	324	885	0.6293	C:\MSD08\MSSEARCH\mainib	638-67-5	-1.0	CSH11	1.2	CAH9	0.3	CTH16	0.9	CSH17
2	Tricosane	C23H48	324	846	0.6283	C:\MSD08\MSSEARCH\mainib	638-67-5	-1.0	CSH11	-0.9	CSH13	0.9	CSH17	0.8	CSH19
3	Tetracosane	C24H50	338	829	0.1200	C:\MSD08\MSSEARCH\mainib	646-31-1	-1.0	CSH11	-0.9	CSH13	0.9	CSH17	0.8	CSH19
4	Tricosane	C23H48	324	823	0.6293	C:\MSD08\MSSEARCH\mainib	638-67-5	-1.0	CSH11	-0.9	CSH13	0.9	CSH17	0.8	CSH19
5	Tetracosane	C24H50	338	818	0.1200	C:\MSD08\MSSEARCH\mainib	646-31-1	-1.0	CSH11	-0.9	CSH13	0.9	CSH17	0.8	CSH19
6	Tricosane	C23H48	324	806	0.1435	C:\MSD08\MSSEARCH\mainib	638-67-5	-1.0	CSH11	-0.9	CSH13	0.9	CSH17	0.8	CSH19
7	Hexacosane	C26H54	354	800	0.0344	C:\MSD08\MSSEARCH\mainib	629-92-2	-1.0	CSH11	-0.9	CSH13	0.9	CSH17	0.8	CSH19
8	Hexacosane	C26H54	366	792	0.0256	C:\MSD08\MSSEARCH\mainib	630-01-3	-1.0	CSH11	-0.9	CSH13	0.9	CSH17	0.8	CSH19
9	Tetracosane	C24H50	338	791	0.1200	C:\MSD08\MSSEARCH\mainib	646-31-1	-1.0	CSH11	-0.9	CSH13	0.9	CSH17	0.8	CSH19
10	Octacosane	C28H58	394	787	0.0207	C:\MSD08\MSSEARCH\mainib	630-02-4	-1.0	CSH11	-0.9	CSH13	0.9	CSH17	0.8	CSH19



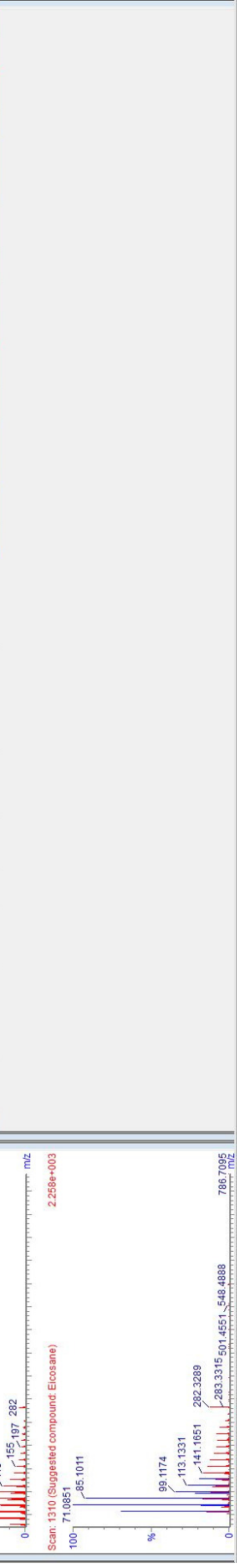


Water (M23) – underivatized

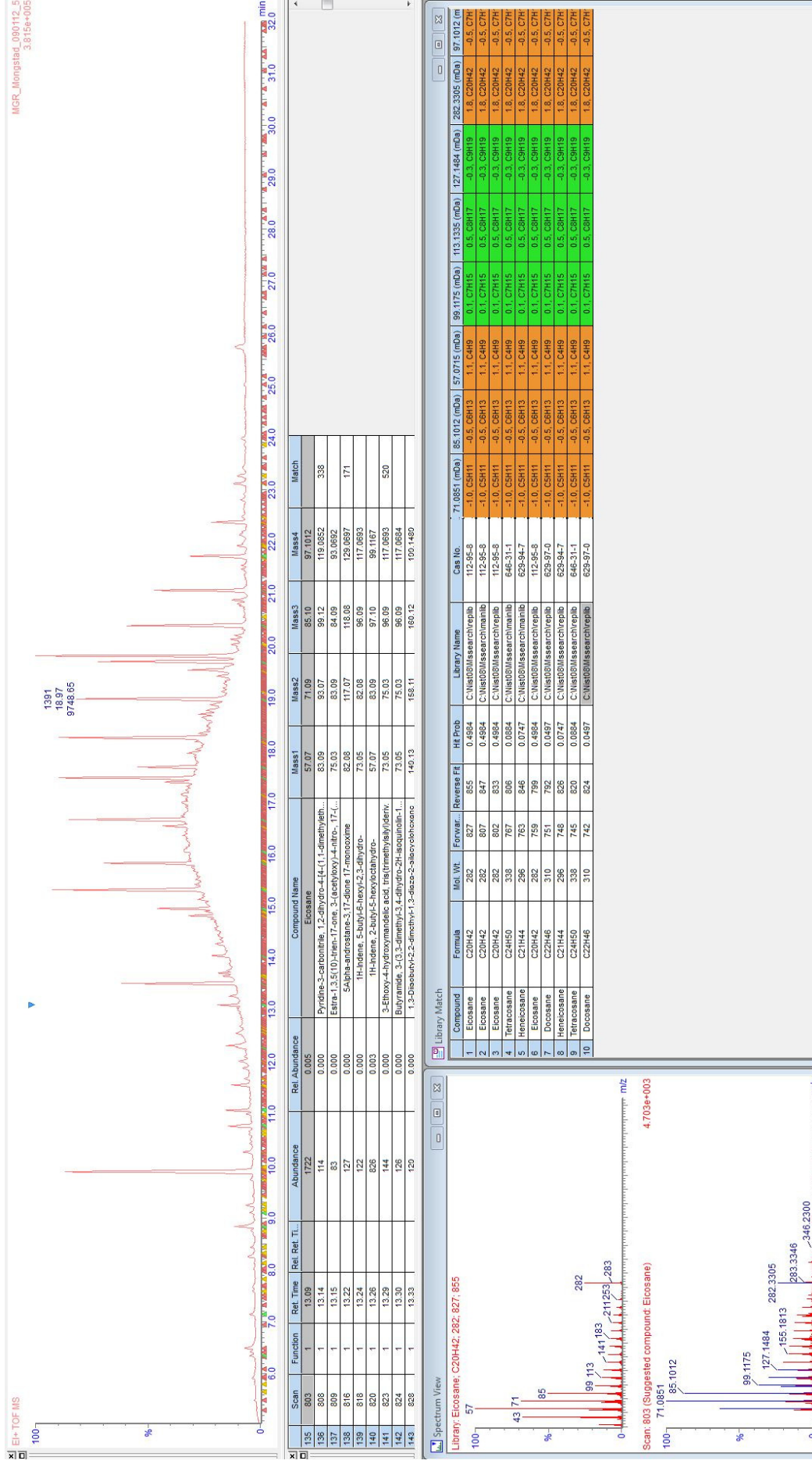


Scan	Function	Ret. Time	Ret. Ret. T.	Abundance	Rel. Abundance	Compound Name	Mass1	Mass2	Mass3	Mass4	Match
28	1	13.10		674	0.943	Eicosane	57.07	69.07	71.09	85.1011	
29	1	13.67		99	0.006	Cyclic octasulfur	63.94	95.92	127.89	159.8502	
30	1	14.95		340	0.022	Docosane	57.07	69.07	71.09	85.0853	
31	1607	1	16.08	16	0.001	Cholestane, 2-formyl-3-(2-methylbenzylidene)-	50.98	81.07	97.10	218.4247	
32	1644	1	16.44	16	0.001	Fumaric acid, propyl 2,4,6-trichlorophenyl ester	55.06	81.07	97.07	99.1158	
33	1653	1	16.54	167	0.011	Hexanedioic acid, bis(2-ethylhexyl) ester	70.08	71.09	111.05	112.1254	
34	1665	1	16.65	155	0.010	Tetracosane	57.07	71.09	85.10	99.1159	
35	1669	1	16.69	48	0.003	1H-Phenanthro[9,10-j]imidazo[2,1-a]pyridine	71.05	88.05	113.06	127.0753	
38	1672	1	16.72	9	0.001	2-Propanoic acid, 1-methyl-	67.06	83.95	85.03	106.0704	

Compound	Formula	Mol. Wt.	Formula	Reverse FI	Hit Prob.	Library Name	Case No.	71.0851 (mDa)	85.1011 (mDa)	57.0714 (mDa)	99.1174 (mDa)	113.1331 (mDa)	97.1011 (mDa)	127.1495 (mDa)	89.0703 (mDa)								
1	Eicosane	C20H42	282	893	0.4376	C:\Nist08MS\search\mainlib	112-95-8	-1.0	CSHT1	-0.6	CRH13	1.0	CAH9	0.0	CPH15	0.1	GRH17	-0.6	CRH13	0.8	CRH19	-0.1	CSH9
2	Eicosane	C20H42	282	873	0.4376	C:\Nist08MS\search\mainlib	112-95-8	-1.0	CSHT1	-0.6	CRH13	1.0	CAH9	0.0	CPH15	0.1	GRH17	-0.6	CRH13	0.8	CRH19	-0.1	CSH9
3	Eicosane	C20H42	282	861	0.4376	C:\Nist08MS\search\mainlib	112-95-8	-1.0	CSHT1	-0.6	CRH13	1.0	CAH9	0.0	CPH15	0.1	GRH17	-0.6	CRH13	0.8	CRH19	-0.1	CSH9
4	Henicosane	C21H44	296	835	0.0915	C:\Nist08MS\search\mainlib	625-94-7	-1.0	CSHT1	-0.6	CRH13	1.0	CAH9	0.0	CPH15	0.1	GRH17	-0.6	CRH13	0.8	CRH19	-0.1	CSH9
5	Henicosane	C21H44	296	835	0.0915	C:\Nist08MS\search\mainlib	625-94-7	-1.0	CSHT1	-0.6	CRH13	1.0	CAH9	0.0	CPH15	0.1	GRH17	-0.6	CRH13	0.8	CRH19	-0.1	CSH9
6	Henicosane	C21H44	296	835	0.0915	C:\Nist08MS\search\mainlib	625-94-7	-1.0	CSHT1	-0.6	CRH13	1.0	CAH9	0.0	CPH15	0.1	GRH17	-0.6	CRH13	0.8	CRH19	-0.1	CSH9
7	Docosane	C22H46	310	831	0.0773	C:\Nist08MS\search\mainlib	629-97-0	-1.0	CSHT1	-0.6	CRH13	1.0	CAH9	0.0	CPH15	0.1	GRH17	-0.6	CRH13	0.8	CRH19	-0.1	CSH9
8	Docosane	C22H46	310	843	0.0607	C:\Nist08MS\search\mainlib	646-31-1	-1.0	CSHT1	-0.6	CRH13	1.0	CAH9	0.0	CPH15	0.1	GRH17	-0.6	CRH13	0.8	CRH19	-0.1	CSH9
9	Henicosane	C21H44	296	821	0.0915	C:\Nist08MS\search\mainlib	625-94-7	-1.0	CSHT1	-0.6	CRH13	1.0	CAH9	0.0	CPH15	0.1	GRH17	-0.6	CRH13	0.8	CRH19	-0.1	CSH9
10	Tetracosane	C24H50	338	814	0.0607	C:\Nist08MS\search\mainlib	646-31-1	-1.0	CSHT1	-0.6	CRH13	1.0	CAH9	0.0	CPH15	0.1	GRH17	-0.6	CRH13	0.8	CRH19	-0.1	CSH9



Water (M23) – derivatised



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