University of Southampton

Development of an autonomous water sampler

By

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ABSTRACT

FACULTY OF ENGINEERING, SCIENCE AND MATHEMATICS

SCHOOL OF OCEAN AND EARTH SCIENCES

Doctor of Philosophy

DEVELOPMENT OF AN AUTONOMOUS WATER SAMPLER

By Athanasios Gkritzalis – Papadopoulos

Aquatic ecosystems are dynamic environments where geochemical, physical and biological characteristics change both spatially and temporally. The timing of these changes can be unpredictable, which makes observation in these environments a difficult and demanding task. Water samplers and monitoring equipment that can work autonomously for long periods and are able to yield high temporal and spatial resolution data, can provide the means to capture changes in aquatic environments. One such example is provided by OsmoSamplers (Jannasch et al. 2004), which are based on the principle of power – free osmotic pumps. Based on the operating principle of existing OsmoSamplers, we have developed an osmotic sampler (Southampton Continuous Autonomous Water Sampler – SCAWS) that uses 12 osmotic pumps (ALZET®) to create an osmotic pressure gradient between a saturated NaCl solution and deionized water. One end of a long and small internal diameter Teflon tube (1mm), filled also with deionized water, is attached to the deionized water compartment and the other end is open to the environment. The osmotic pressure gradient draws ambient fluids into the sampling tube where the samples are stored. After recovery the sampling tube is cut into segments, with each segment representing a specific sampling period (e.g. daily sample). The sampling rate of osmotic samplers depends on temperature and for the SCAWS it ranges from 0.8 ml/d to 2.4 ml/d. In order to account for this effect, the SCAWS is equipped with a mechanism that time stamps the samples (tracer addition via a microsolenoid pump), which helps to segment the sampling tube more accurately. Sampling can also be compromised by aggregate matter that might enter the sampling tube and potentially block it, especially when the sampler is deployed in environments with high concentrations of suspended matter (e.g. rivers, estuaries). For this reason a custom made filtering system equipped with a renewable 1μm nylon mesh is installed at the sampler's inlet. Two prototypes of the SCAWS were deployed in a local marine and river environment for periods ranging from one week to one month. During the deployments manual samples were collected, against which the samples collected from SCAWS were compared. All samples were analyzed with Ion Chromatography for the determination of major anions and cations, and also with ICP-MS for further determination of the major cations and a suit of trace metals. The results indicate that the SCAWS performed well in being able to capture transient events and preserve geochemical signatures during storage. With further technical development of the sampler and optimization of the innovative parts performance, the SCAWS has the potential to be a more robust and versatile instrument, able to sample fluids in a variety of aquatic environments.

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DECLARATION OF AUTHORSHIP

I, Athanasios Gkritzalis – Papadopoulos

declare that the thesis entitled

"Development of an autonomous water sampler"

and the work presented in the thesis are both my own, and have been generated by me as the result of my own original research. I confirm that:

- this work was done wholly or mainly while in candidature for a research degree at this University;
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- where I have consulted the published work of others, this is always clearly attributed;
- where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;
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- none of this work has been published before submission

Signed: ……..

Date:…….

BIOTRACS

Bio-transformations of trace elements in aquatic systems

Marie Curie Actions

Early - Stage Training (EST) Fellowship

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Every journey has a start. Even though the PhD started a bit more than three years ago, this scientific journey started in Athens – Hellas, some 15 years ago. My guide was Dr. Antonis Megalopoulos; an exceptional scientist, a great teacher, an accomplished businessman, my uncle. His teachings and guidance through most of my academic and professional life was such that led me to pursuit science and to work in scientific and parsimonious way. For that I feel blessed and privileged, and I strongly believe that without his guidance my scientific eyes would have never opened. I would like to thank him for all the help and support he has provided.

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Dedicated to Theodore and Gina for their love

January 2009

T.G

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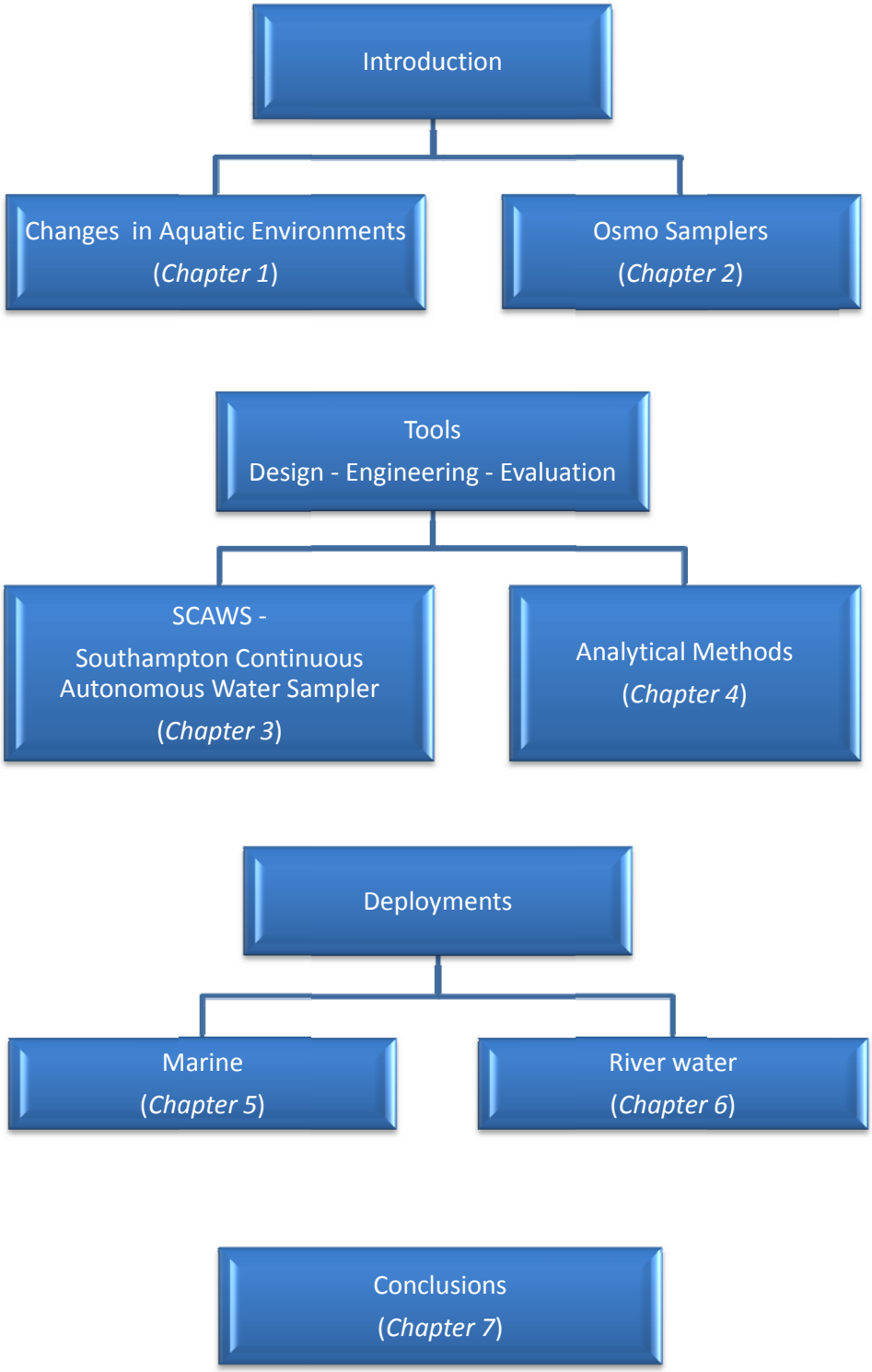


1 Changes in Aquatic environments

The chemical composition of aquatic environments is constantly changing. These changes can be caused by natural phenomena (e.g. vertical water motion, earthquakes), climatic events (e.g. El Nino), or human activities (e.g. pollution). In many cases these changes are unpredictable and irregular; hence they are unlikely to be captured on a single expedition, cruise or field trip. Considering, as well, that in many aquatic environments accessibility is restrained by climatic conditions, ship and personnel availability, it is easy to understand why observing and studying aquatic environments is a difficult, very demanding and expensive task. However, it is very important to record and study these changes in order to have a better picture of these environments. In addition, environmental degradation and climate change are now important social issues, so it is imperative to understand processes in aquatic environments and how these environments respond to changes (Bates *et al.*, 2008).

1.1 Riverine systems

The importance of rivers on global biogeochemical cycles and on the environment is well documented in literature (Gibbs, 1970; Garrels and Mackenzie, 1971; Meybeck, 1987; Drever, 1988; Palmer and Edmond, 1989, 1992, 1993; Berner and Berner, 1996; Huh *et al.*, 1998; Meybeck, 1998; Peters and Meybeck, 2000; Vorosmarty *et al.*, 2000; Huh *et al.*, 2001; Meybeck, 2002; Pahl-Wostl *et al.*, 2002; Meybeck, 2003). Large river basins, have been given great attention, because of their importance on global biogeochemical cycles. The Amazon basin (Edmond *et al.*, 1981; Stallard and Edmond, 1981, 1983, 1987; Berner and Rao, 1994; Tardy *et al.*, 2005; Roddaz *et al.*, 2006), the Indian basin rivers (Sarin and Krishnaswami, 1984; Chakrapani, 2005) the Yangtze (Hu *et al.*, 1982; Milliman *et al.*, 1983; Chen *et al.*, 2002; Muller *et al.*, 2008) and basically most of the large river catchments, have been studied extensively for their geochemical characteristics, their relationship with physicochemical processes (denudation rate, sediment transport, temperature variations, etc.) and with anthropogenic activities (atmospheric CO_2 inputs, domestic, agricultural and industrial inputs – pollutants).

All the above studies (and numerous others that are not mentioned) produced invaluable results and gave fundamental insights of river water biogeochemistry.

In many of them it is emphasized that more frequent water sampling and monitoring, will definitely increase our knowledge of these systems and give a more complete (perhaps different?) picture of these environments. However, in view of the high costs associated with undertaking these sampling expeditions, how can this be best accomplished?

One reason that constrains our ability to study these environments on a regular and frequent basis is their immense size and the fact that they often lie in very remote and difficult to access areas. Clearly, the financial and logistical demands for continuous expeditions are very high, and it is equally obvious how difficult it is to establish stations that will provide the necessary support for the necessary monitoring and sampling equipment (a brief presentation of the available equipment is given in section 1.3.2).

It is relatively easier to carry out such studies in medium and small river catchments (Johnson *et al.*, 1969; Robson *et al.*, 1992; Robson *et al.*, 1993; Moldan and Cerny, 1994; Peters *et al.*, 2006). Such environments can provide the means to study environmental conditions and identify spatial and temporal environmental patterns. Research can be carried over a very long period of time (for example, Hubbard Brook Valley Ecosystem Study was established in 1955 and still produces high quality research). Within these experimental catchments it is possible to establish long term monitoring stations, where fluvial geochemistry and physical parameters can be monitored at much higher frequency. This allowed researchers to "quantify" the importance of high frequency sampling and monitoring in relation to the interpretation of geochemical and environmental indices (Jarvie *et al.*, 2001; Alewell *et al.*, 2004; Kirchner *et al.*, 2004; Soulsby *et al.*, 2008). This is illustrated in Figure 1-1, where conductivity records, obtained at different sampling intervals, indicate the loss of information when conventional sampling strategies are applied (monthly, weekly and even daily). Given that a strong relationship generally exists between conductivity and concentration of dissolved matter, it is probable that information of the fluvial geochemistry can also be obscured by low frequency sampling.

Therefore, it is necessary to use water sampling and monitoring equipment that is capable of operating at high frequency intervals, which are customised to the characteristics of the catchment and can minimise the uncertainties in our estimations. The development of autonomous long term operating devices (samplers and sensors), will allow for the advance of novel research on river water geochemistry.

It is also necessary that such equipment will start being used for research in major river basins. Even though many research programs focus on these basins, the data collection frequency is usually low and in most cases sporadic. Defining the fine structure of changes in major river systems is essential in order to get a better and more refined picture of the role of major rivers on geochemical cycles. High temporal resolution data will give the opportunity to capture transient geochemical events of high order of magnitude and identify their impact on the ecosystems.

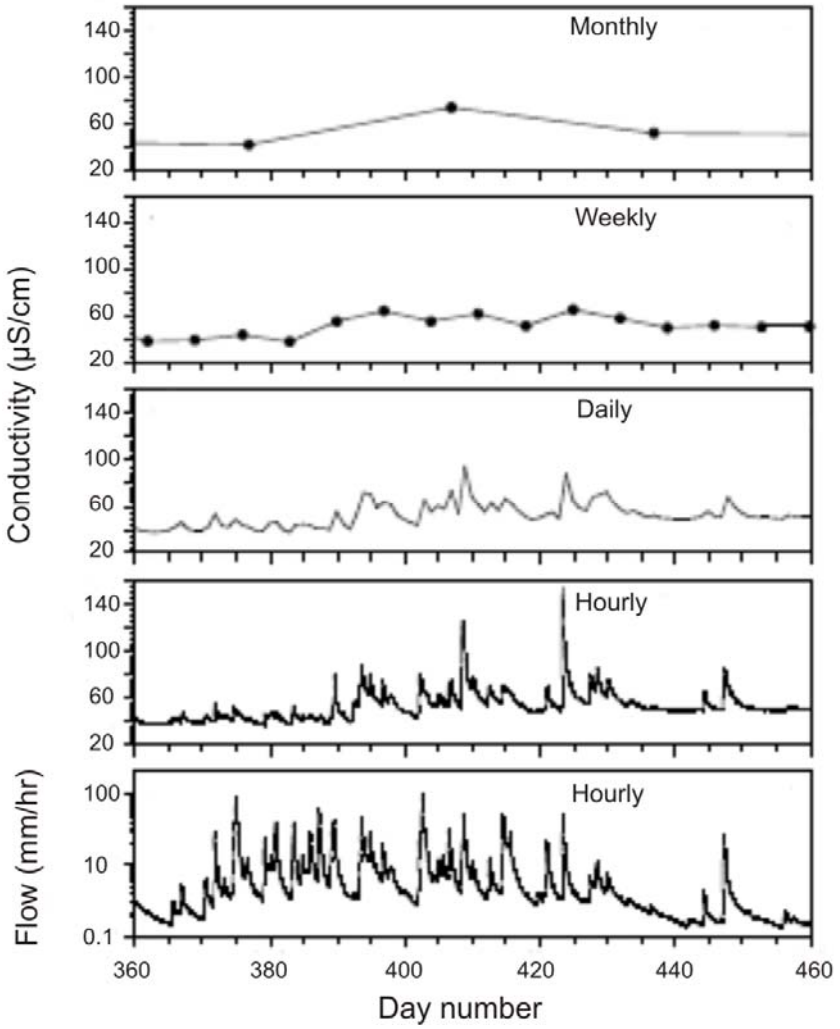


Figure 1-1: Significance of high frequency sampling – monitoring resolution to hydrological and geochemical parameters. (Kirchner *et al.*, 2004)

1.2 Marine environments

Dave Karl (1999) noted that *"For the organisms that inhabit the North Pacific Subtropical Gyre, nothing is constant except change and nothing is certain except stratification of the water column, low nutrient and low biomass"*. Many years of marine and oceanic research have suggested that this is true for all oceanic environments. Considering the significance of the oceans on the control of the earth's system and the importance of climate change, it is easy to understand the need to capture temporal changes in marine environments (coastal and oceanic).

Of course this is much easier said than done. Environmental conditions and accessibility of these environments can (in many cases) compromise the desired outcome. Equipment failure due to biofouling and corrosion, or loss of equipment due to unpredicted parameters (e.g. equipment destroyed by fishing lines or trawling) is a common fact for marine research. However, the

increasing needs to study marine environments in a holistic manner has led to the establishment of long – term marine observatories (coastal and oceanic).

In 1978 the Oceanic Flux Programme (OFP) (Deuser and Ross, 1980; Deuser *et al.*, 1988; Conte, 1997) was established in Bermuda by the Woods Hole Oceanographic Institute. Its main purpose is to measure particle fluxes in the ocean and evaluate their temporal variability. In 1988 the Joint Global Ocean Flux Studies (JGOFS) programme was established and within it various long term monitoring programmes started their operation. The major programmes of JGOFS are the Hawaiian Ocean Time Series (HOTS) (Karl and Lukas, 1996) and the Bermuda Atlantic Time Series (BATS) (Michaels and Knap, 1996; Steinberg *et al.*, 2001). The main purpose of both programmes was to investigate, in a holistic manner, marine environments in the Atlantic and Pacific Ocean, compare data, and identify biogeochemical and physical patterns. These programmes were a major breakthrough in ocean sciences and continue to produce important data for oceanography.

In Europe, over the past 20 years a number of observatories were developed and recently the European Union, funded a project (EuroSITES, see Figure 1-2) where 9 deep sea observing stations will combine forces to establish a powerful network for long term marine research. The concept behind this project is to develop marine observatories that will provide the necessary means to understand temporal patterns of marine environments. An essential part of this project is the deployment of the necessary equipment and technology to address its targets.

Figure 1-2: EuroSITES network for long - term marine observatories (www.eurosites.info).

For all long term marine observation programmes, frequent sampling is necessary to build up meaningful long term data sets. However, in most cases water samples are only collected during visits - monthly or less frequently - of the support research ship. This sampling frequency helps scientists to draw general conclusions on temporal variability but it limits opportunities to capture

unpredictable events. Various in situ analyzers and water samplers have been used to try to fill this temporal gap of geochemical observation. Some examples are presented in the following sections.

1.3 Capturing Changes: Sampling and Monitoring

From the above review, it is clear that there is a strong need to capture changes in aquatic environments. The means to fulfil this need are in no way simple. The challenges that such tasks entail demand the meticulous preparation of all the task's aspects. Knowledge of environmental conditions, availability of personnel and their suitability to the task, and the technical means to capture changes, must be well defined in order to get a better picture of the environment.

1.3.1 Water sampling requirements for environmental studies

In the chain of activities that are associated with water analysis, sampling is the initial link, which is frequently the weakest one. Errors during sampling are permanent and cannot be rectified or compensated. Hence, subsequent results will not represent the sites true condition. The errors that can be entailed during sampling, and their importance against other parameters that are related to environmental data production are conceptualized in Figure 1-3 (Keith *et al.*, 1996).

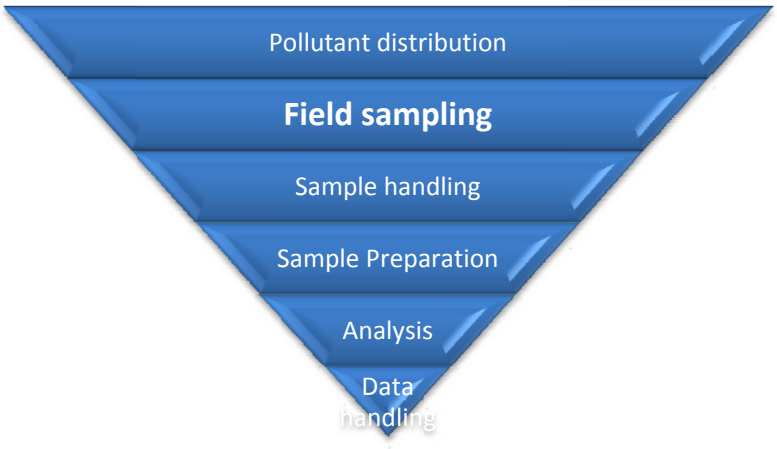


Figure 1-3: Sources of variability for environmental data acquisition (Keith *et al.*, 1996).

Worsfold (2006) has identified the importance of high quality data and the interaction between parameters that are connected to high quality analytical chemistry data. These are illustrated in Figure 1-4.

Combining the concepts of Figure 1-3 and Figure 1-4, we can identify the importance of sampling procedures on the production of high quality data. Because of this importance sampling procedures must follow protocols which can assure consistency on sampling procedures and limit mistakes.

The minimum requirements for sampling procedures, as suggested by the American Chemical Society Committee on Environmental Improvement (Macdougall *et al.*, 1980) are:

- Proper Statistical design that takes into account the goals of the studies and its certainties and uncertainties
- Instructions for sample collection, labelling, preservation, and transport to the analytical facility
- Training of personnel in the sampling techniques and procedures

Sampling may seem like a trivial and straight forward process, but the complex and unstable nature of aquatic environments, and the variable conditions at sampling sites, prove the opposite. For most environmental applications sampling procedures have been standardized, and in many cases legally regulated. This often is the case in programmes and applications that are related with human health and water management. Sampling equipment, whether it is a simple bottle or a sophisticated autosampler, is a vital part of the sampling process.

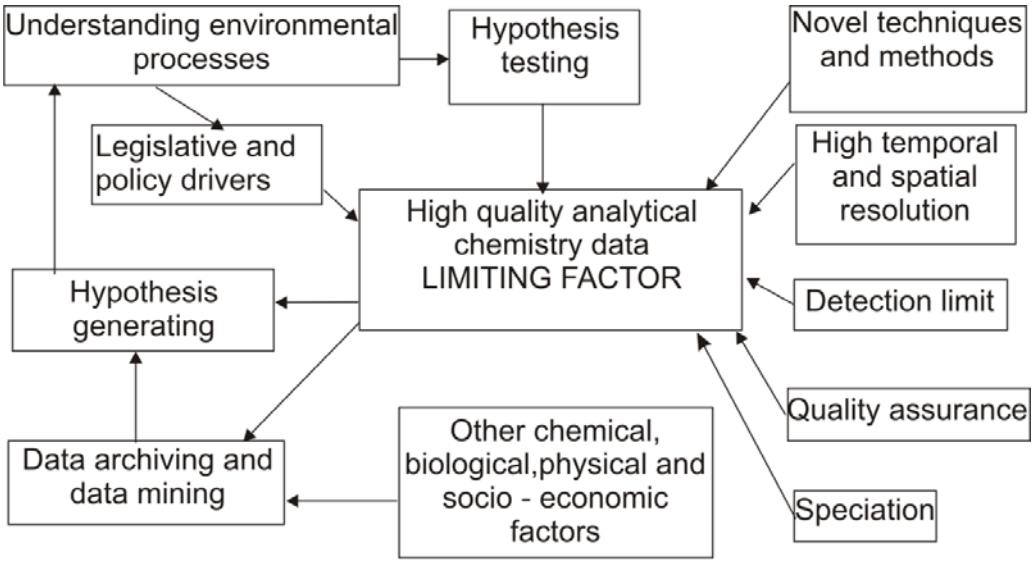


Figure 1-4: Importance of high quality analytical data and interaction with other parameters (Worsfold, 2006).

1.3.2 Water sampling and monitoring equipment for environmental studies

1.3.2.1 Water Samplers

Water samplers come in direct contact with the sample, and can affect the sample's integrity and representativeness. Sampling equipment should not affect the concentration or characteristics of the chemicals of interest. Hence, all the material that comes in contact with the sample should be inert (no leaching, or absorbing properties). Operation and maintenance of samplers should be simple so that multiple users can operate them and always provide representative samples. The type of

sampler often needs to be specifically tailored to the environment. For example different techniques will be used for sampling drinking water and wastewater. Chemicals of interest and analytical techniques have to be considered for the selection of the proper sampling procedures and equipment. Spatial and temporal variability of the examined environment also play an important role on the selection of the sampling equipment, especially for in-situ long term samplers. Water samplers must also be consistent, so that any inherent errors are identified at early stages of the sampling process and taken into account during the next stages.

Long term monitoring programmes require specialized monitoring and sampling equipment that meets the demands of the programme. Conventional sampling equipment, like the Niskin bottle, is not suitable for long term monitoring programmes, as it cannot be deployed for a long period of time. Specialized samplers that are used in long term monitoring programmes are discussed below.

The moored in situ trace element serial sampler (MITESS) for deep-sea moorings (see Figure 1-5 A) is a long term in situ water sampler designed especially for trace metal sampling (Bell *et al.*, 2002). The sampler is moored at a specific depth and at predetermined times the sampling bottle is opened and filled with seawater. Acid is used to flush the sampling bottles and preserve the samples. MITESS has been successfully deployed in Bermuda Testbed Mooring and in Hawaii Ocean Time Series site. It should be noted that the MITESS has a limited temporal sampling resolution, as it depends on the number of sampling bottles that are installed. For example, for a seven month deployment the sampler collected sixteen samples. The Remote Access Sampler (RAS) developed by McLane research laboratories (see Figure 1-5 B) is similar to the MITESS sampler. Maximum deployment period is 18 months and they can collect up to 48 samples of 100ml or 500ml. RAS samplers like MITESS are reliable, but their temporal resolution is rather limited for the same reason as the MITESS. Sampling times have to be preset, which means that the samplers might not sample unpredicted events. Also such samplers are usually very expensive.

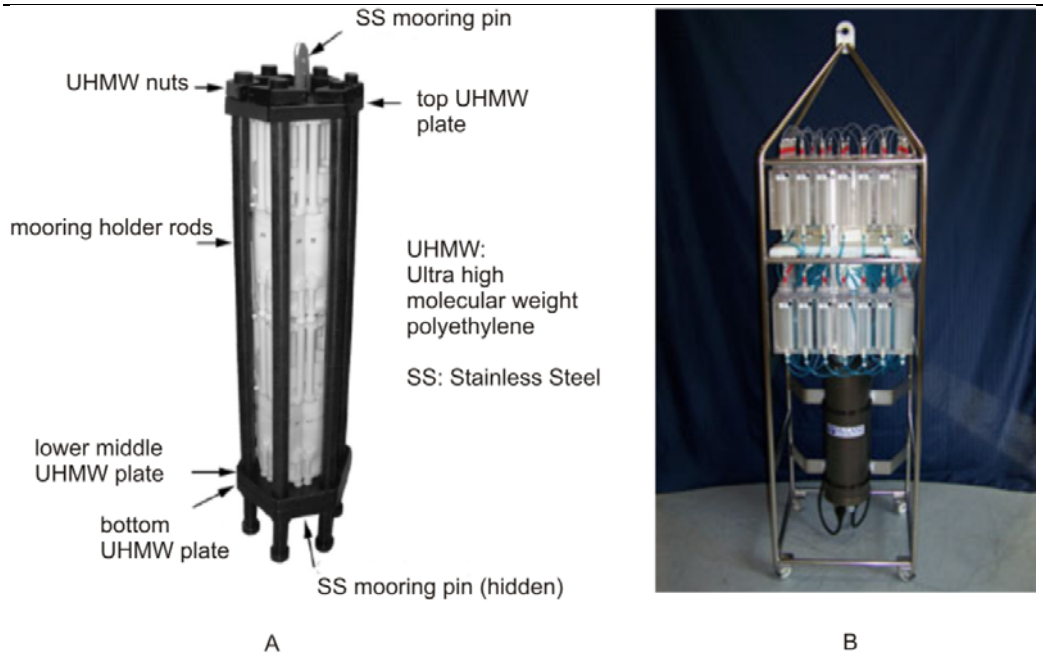


Figure 1-5: Long term water samplers. A: Moored In situ Trace Element Serial Sampler (MITTES) (Bell *et al.*, 2002); B: remote access sampler (Mclane research Laboratories, www.mclanelabs.com)

Automatic samplers like the one illustrated in Figure 1-6, are used extensively for wastewater sampling and easy to access terrestrial aquatic environments. These samplers are used mainly by wastewater treatment facilities and water companies. They require power and personnel support to operate, which makes them unsuitable for remote areas sampling applications, where long term autonomous sampling is required.

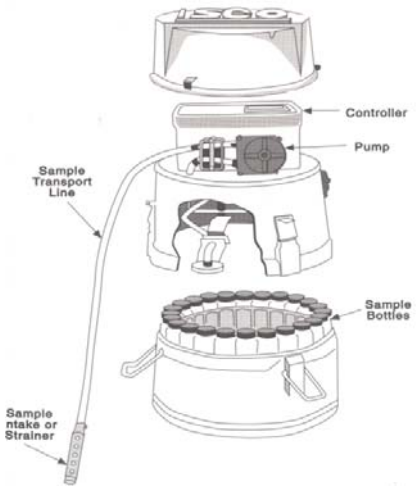


Figure 1-6: Automated water - wastewater sampler (Dick, 1996).

1.3.2.2 In situ sensors – Monitoring equipment

Over the past 30 years, technology for in – situ sensors and analysers for aquatic chemistry has developed significantly. Such devices offer major advantages, but at the same time entail inherent challenges.

The major advantage of in-situ devices for determination of analytes is that they provide very fast and continuous results. An additional advantage of this technology is that it reduces uncertainties that are related to the production of analytical data (see Figure 1-3), as the stages of Field Sampling, Sample Handling and Sample Preparation are eliminated. Provided that the errors of the analytical component are within the desired limits, in-situ sensors seem to be ideal for monitoring and research purposes.

The most common sensors that have been used so far, and with a great degree of success are the ones for pH and conductivity/salinity. Technological advancement in analytical methods (and especially electrochemistry) and the need to monitor water resources, led to the development of sensors for the on-line monitoring of pollutants and other chemical species. Today there are several companies that manufacture and provide sensors for, nitrate, oxygen, ammonia, phosphate, organic species, fluorescence etc. (e.g. YSI Hydrodata, Idronaut, WTW, Prominent, Hach), which are used for monitoring of marine environments (YSI, Idronaut), fresh waters and wastewaters (WTW, Prominent, Hach). However, certain limitations restrict the use of this technology to remote environmental monitoring. The main one is that these sensors/analysers require electrical power to sustain the operation of their electronics, which reduces the period that they can operate autonomously. Another issue that may compromise the operations of such devices is that most electrochemical or photochemical sensors are delicate instruments that may be influenced by biofouling (biofilm creation around electrodes or optodes), resulting in loss of sensitivity and false data. Moreover, such devices have a limited analytical spectrum, which means that they can only offer information on specific analytes and collection of samples for laboratory analysis is still required if a complete picture of the site is required. Last but not least these sensors entail high costs (purchase and maintenance).

Apart from the above mentioned sensors, the technology of diffusive gradient thin films (DGT) and diffusive equilibration thin films (Zhang *et al.*, 1998; Fones *et al.*, 2001; Dahlqvist *et al.*, 2002; Peters *et al.*, 2003; Dočekalová and Divis, 2005) is becoming more popular in environmental monitoring and geochemical research. The DGT/DET technology emerged almost fifteen years ago and is still developing and expanding its application spectrum (Monbet *et al.*, 2008; Pichette *et al.*, 2009). The big advantage of this technology is the continuous and power-free sampling of a variety of aquatic environments (marine, freshwater, sediment pore waters). In addition DGT/DET technology is suitable for speciation studies, which no conventional sensors or long term monitoring sensors can offer.

1.4 Overview - Aim

"Clearly the accuracy with which we can determine riverine fluxes is not limited by analytical techniques, but is inherently restricted by the natural variability in the rivers themselves and the problems of obtaining representative long-term data series"(Palmer and Edmond, 1989)

"… in order to obtain information on the intra annual variability of the major ion composition, water samples have to be taken at regular intervals, preferable during an entire year" (Smolders et al., 2004)

"Routine stream monitoring is rarely carried out for scientific purposes… Infrequent events of short duration can provide most of the sediment transport; thus long densely sampled time – series are required to obtain accurate estimates" (Edmond et al., 1995)

"Imagine trying to understand a Beethoven symphony if one could only hear one note every minute or two! That is what we are trying to do when we infer the hydrochemical functioning of a catchment from weekly or monthly grab samples. Or imagine trying to understand a symphony from a high-fidelity recording of just one of its crashing crescendos. That is what we are trying to do when we analyse high-frequency samples of an individual storm event. Continuous high-frequency monitoring of catchment hydrochemistry will require significant resources and tenacity. In our view, however, what we stand to learn is well worth the effort. If we want to understand the full symphony of catchment hydrochemical behaviour, then we need to be able to hear every note." (Kirchner et al., 2004)

"Chronic undersampling, a fact of life in oceanography, constrains the interpretation of field data. Neither spatial heterogeneity nor temporal intermittency are measured well by shipboard sampling, and the dimensions and dynamics of North Pacific gyre preclude comprehensive sampling." (Karl, 1999)

The above quotes are just a few that illustrate the need for high frequency temporal resolution of sampling and monitoring of aquatic environments. Some of the devices that can facilitate this need were presented earlier in this chapter. From this presentation, it is clear that autonomous water samplers operate only at predetermined moments, and can only collect a limited amount of samples, so it is possible for sporadic and random events to be lost.

In the case of high frequency monitoring systems (equipped with sensors) monitoring is restricted to one or few analytes, which cannot give a holistic geochemical picture of the environment. In addition to the above, power requirements, robust unattended operation and in many cases excessive cost (purchase and maintenance) are questions that are still looking for answers.

Identifying this gap in water sampling equipment, this project attempts to give an insight and explore the potentials of a relatively new and promising technology that can give solutions to some of the challenges that are related to long term, continuous, autonomous water sampling. The following chapters are dedicated to the OSMO SAMPLING technology, its applications and a

suggestion for a water sampling device that has the potential to become a powerful tool in the water research arsenal

2 Osmo Samplers

2.1 Osmotic pumps and Environmental applications

From the previous chapter it is clear that aquatic environments are under sampled, both spatially and temporally. One of the reasons, for this is that the available sampling and monitoring equipment does not have the ability to operate autonomously and continuously for long periods (days to months).

The main challenges for unattended and autonomous long term sampling and monitoring equipment are related to:

- power requirements of parts including, motors, pumps and valves,
- biofouling of the device which can compromise its operation.

Batteries can provide the necessary power requirement, but longevity and efficiency demand large battery packs that increase both the size of the instrument package and the cost. In addition any technical problems with the batteries will more than likely lead to fast power drainage and compromise the sampling/monitoring process. Alternative power sources (e.g wind, solar, waves) for sampling and monitoring equipment are commercially available but tend to be expensive and may not be applicable to all environments e.g solar lights cannot be used in low light environments.

Biofouling is a reality for all equipment that is deployed for extended periods in aqueous environments. The available treatments (disinfectants and biocides) can only delay biofouling and not prevent it. Research on new materials that is resistant to biofouling is still at an embryonic stage and, so far, they are not commercially available.

These observations indicate that an ideal device for sampling and monitoring aquatic environments would be able to operate with minimal power requirements and be biofouling free. Closer examination of some of the equipment that described in section 1.3.2 shows that one of the crucial parts of the sampling device, and probably the one with the highest power consumption, is the pump that collects the sample or delivers the sample to the “sensor”. Therefore alternative pumping devices with low power consumption and long operating lifetimes are necessary.

Based on this concept, Hans Jannasch, Ken Johnson and their scientific team in Monterey Bay Aquarium Research Institute (MBARI), developed instruments that use osmotic pumps instead of conventional pumps (Jannasch *et al.*, 1994; Jannasch *et al.*, 1998; Kastner *et al.*, 2000; Wheat *et al.*, 2000; Chapin *et al.*, 2002; Jannasch *et al.*, 2004). The use of osmotic pumps in these devices, reduces significantly, and in some cases eliminates completely, the electrical power requirements. Therefore, instruments that use osmotic pumps can be deployed for long periods. The principle behind the operation of osmotic pumps and a brief description of the instruments that use them are presented below.

2.2 Osmotic pumps

2.2.1 Principles of Osmosis

The operation of the osmo sampler depends on the osmotic gradient that is created when two solutions with different ionic concentrations are separated by a semi permeable osmotic membrane. Semi permeability is defined as the ability of the membrane to allow flow molecules of certain size. Therefore, if a high solute concentration solution is separated from a low solute concentration solution by a semi permeable membrane that only allows passage of molecules with sizes similar to water, then water molecules will pass through the membrane, until ionic equilibrium is reached (Figure 2-1).

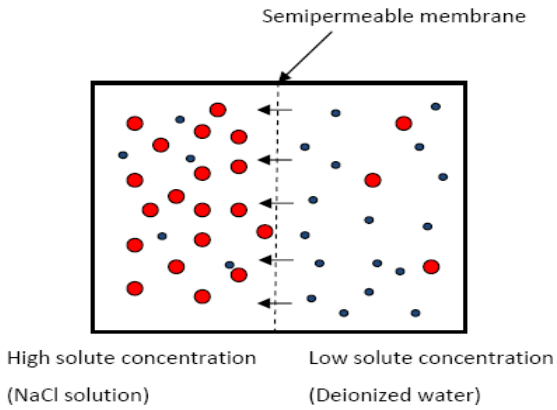


Figure 2-1: Principle of osmosis.

A fundamental property of osmosis is the pressure gradient that is created across the membrane as a result of differences in ionic strength of the two solutions. The osmotic pressure was first studied by Van't Hoff (Van't Hoff, 1888) who described osmosis using equation 2-1.

$$\pi = C \cdot R \cdot T \qquad \textbf{2-1}$$

Where π is the osmotic pressure (N/m^2) of a solution, C is the concentration of a solution (mol/m^3), R is the ideal gas constant (8.314472 $N \cdot m \cdot K^{-1} \cdot mol^{-1}$), T is the temperature (K).

The flow rate of the liquid across the osmotic membrane can be obtained from equation 2-2

$$J = A \cdot L_p \cdot (\sigma \cdot \Delta\pi - \Delta P)$$
$$\Delta\pi = \pi_s - \pi_o \qquad \textbf{2-2}$$
$$\Delta P = P_s - P_o$$

Where J is the volume flux of solution transported through the membrane per unit of time (m^3/h), A is the effective surface area of the osmotic membrane (m^2), L_p is the permeability of the membrane to water ($m^3/N \cdot hr$), σ is the osmotic reflective coefficient of the membrane, Δπ (N/m^2) is the

osmotic pressure difference across the membrane, where π_o is the osmotic agent (high concentration) and π_s is the osmotic pressure of the solution outside the semi permeable membrane (low concentration) and ΔP (N/m^2) is the hydraulic pressure difference across the membrane. Because the difference in hydraulic pressure ($\Delta P \approx 0$) is negligible (see section 3.2.2), equation 2-2 becomes:

$$J = L_p \cdot A \cdot \sigma \cdot \Delta\pi \qquad \textbf{2-3}$$

Continuous flow rate through the osmotic membrane is maintained as long as $\pi_s > \pi_o$.

An important parameter is the membranes reflection coefficient, σ. This parameter is a measure of the semi – permeability status of the membrane. As long as $\sigma \approx 1$ the osmotic pressure gradient that is created across the membrane generates a flow across the membrane as a mechanical pressure difference of equal magnitude but of a different sign (Mauro, 1960). The reflection coefficient (σ) depends on:

- the solute concentration (Adamski and Anderson, 1983).
- and the membrane material (Theeuwes, 1975).

Another important feature of osmosis is the dependence of the osmotic pressure with temperature. Equation 2-1 indicates that osmotic pressure has a linear relationship with temperature, with positive correlation. The effect of the temperature on the flow rate across the osmotic membrane will be studied in sections 2.2.4 and 3.3.1.

2.2.2 General Description

Based on the above principles, Theeuwes, on behalf of ALZET® corporation, designed and manufactured osmotic pumps that could be used as autonomous drug delivery systems (Theeuwes, 1975; Theeuwes and Yum, 1976). The basic concept of the osmotic pump is illustrated in Figure 2-2.

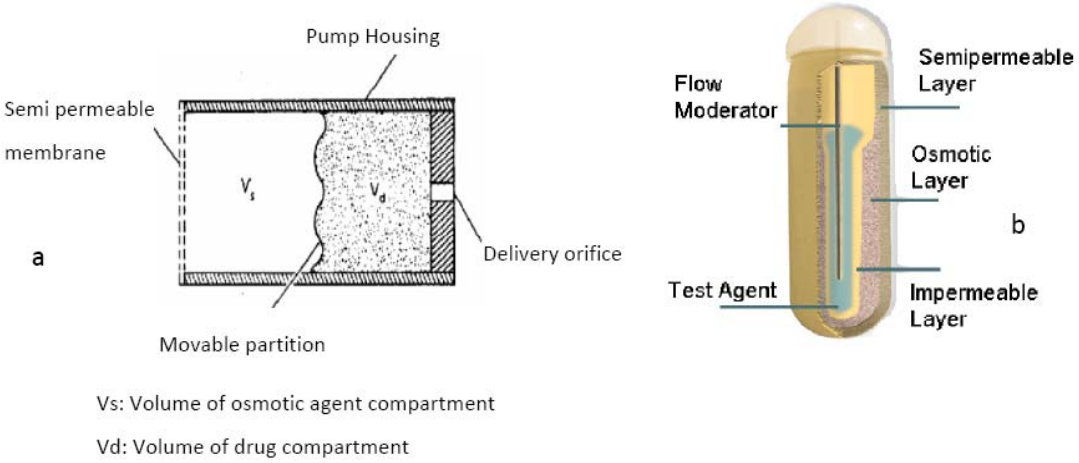


Figure 2-2: Osmotic pumps; a) Basic Concept of osmotic pumps, b) Alzet® 2ML1 osmotic pumps.

The osmotic pumps are used as *in situ – in vitro* drug delivery systems, for tests in animals. The osmotic gradient is created between the blood of the animal and the osmotic agent that is behind the semi permeable membrane. The drug compartment is a collapsible impermeable membrane (bladder) that is squeezed when blood enters the osmotic layer. The pressure that is created on the movable partition, forces the drug through the delivery orifice into the blood stream. The life span of the pump depends on the solubility of the osmotic layer to the ambient fluid (e.g. deionized water, blood), the size of the drug compartment and the ability of the osmotic membrane to retain an osmotic reflection coefficient close to unity for the duration of the experiment.

The basic characteristics of an Alzet® osmotic pump are listed in Table 2-1

Length (cm)	5.1
Diameter (cm)	1.4
Weight (g)	5.1
Membrane material	Cellulose ester blend
membrane thickness (mm)	~ 1.0
Osmotic layer	NaCl

Table 2-1: Alzet® 2ML1 pump characteristics

It should be noted that ALZET® was the first company to develop this type the osmotic pumps and has patented the pumps and developed products with various delivery rates for various applications. A preliminary investigation of the osmotic pumps market indicated that there are no other major manufacturers and suppliers of osmotic pumps. There are a few research institutes that develop and manufacture osmotic pumps (e.g. State of Utah Center of Excellence for Biomedical Microfluidics) but they are using their products to conduct their own research and do not market them.

2.2.3 Delivery Rate

According to Theeuwes (1975) the delivery rate of the elementary osmotic pump is zero order from t = 0 until a critical time t_z and it can be described by the equation 2-4.

$$\left(\frac{dm}{dt}\right)_z = A \cdot \not{k} \cdot \pi_s \cdot S \qquad \textbf{2-4}$$

Where $(dm/dt)_z$ is the zero order delivery rate (g/hr) from time t=0 to time t = t_z, $\not{k}$ replaces the product $L_p \cdot \sigma$ (m^3/N·hr), S is the saturation concentration of the osmotic agent (g/m^3) and π_s is the osmotic pressure of the solution when it is supersaturated (N/m^2).

The zero order delivery time (t_z) can be obtained by the following equation (Theeuwes, 1975)

$$t_z = m_t \cdot \left(1 - \frac{S}{p}\right) \cdot \frac{1}{\left(\frac{dm}{dt}\right)_z} \qquad \textbf{2-5}$$

$$m_t = p \cdot V$$

Where, m_t is the osmotic agent mass contained in volume V (m^3) of the osmotic pump and p is the density of the osmotic fluid (g/m^3).

After $t = t_z$ the delivery rate of the osmotic pump is calculated from

$$\frac{dm}{dt} = \frac{\left(\frac{dm}{dt}\right)_z}{\left[1 + \frac{1}{S \cdot V} \cdot \left(\frac{dm}{dt}\right)_z \cdot (t - t_z)\right]^2} \qquad \textbf{2-6}$$

Equation 2-6 indicates that after the time t_z the delivery rate follows a parabolic decline, which is related to the dilution of the concentration C, from water entering the osmotic pump.

The overall delivery rate of an elementary osmotic pump is presented in Figure 2-3. As can be seen from Figure 2-4 the operating period of modern Alzet® osmotic pumps has significantly increased from early models. According to ALZET® the osmotic semi – permeable membranes used in their osmotic pumps retain their characteristics for up to 5 years (σ remains equal to 1). Therefore if the concentration of the osmotic agent is kept at levels that retain the osmotic gradient, the pumps will provide a continuous constant flow rate over this period.

From both figures it is evident that the delivery rate of the pumps is very low. From information gathered from ALZET®, delivery rates, for most commercial osmotic pumps range from 0.11μL/hr to 10μL/hr.

The semi permeable membrane of the osmotic pump is made from a cellulose ester blend, the collapsible bladder is made from a thermoplastic hydrocarbon elastomer, and the osmotic layer is usually a salt with high solubility to water (NaCl) glued to the inner surface of the membrane.

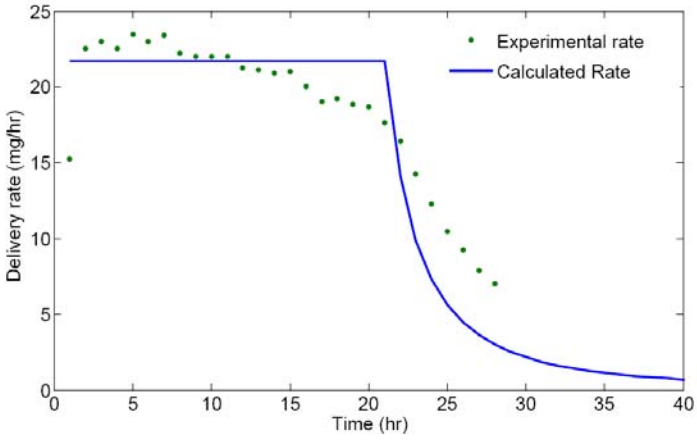


Figure 2-3: In vitro release rate of KCl from elementary osmotic pumps (Theeuwes, 1975).

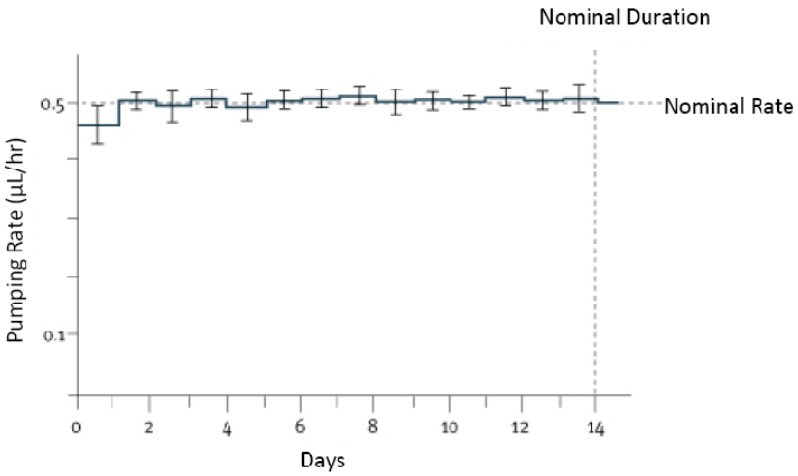


Figure 2-4: Pumping rate of ALZET® 2000 osmotic pump. (http://www.alzet.com/products/performance.php)

2.2.4 Delivery Rate and Temperature relationship

The concentration distribution of a solute that crosses a membrane is given by the following equation (Adamski and Anderson, 1983)

$$C(x) = C_{\infty} \cdot e^{-E(x)/kT}(1 + b_1(x)C_{\infty}) \qquad \textbf{2-7}$$

Where *C(x)* is the solute concentration inside the membranes pore (mole/m^3), C_{∞} is the solute concentration in bulk solution in equilibrium with the pore fluid (mole/m^3), *E(x)* is the energy of one solute particle whose center is at point x (J) and $b_1(x)$ is an integral involving particle energies *E(x)* and *U(x)* (m^3/mole).

Combination of equations 2-7 and 2-4, indicates that there is an exponential relationship between the osmotic pumps flow rate and temperature.

ALZET® suggests an exponential relationship between temperature and delivery rate of the osmotic pump, which is given by the following equation:

$$Q = Q_0 \cdot (0.141 \cdot e^{0.051 \cdot T} - 0.007 \cdot \pi + 0.12) \qquad \textbf{2-8}$$

Where Q_0 is the specified pumping rate at 37 °C (µl/hr), T is the temperature (°C) and π is the osmotic pressure of the solution outside the membrane (atm). Equation 2-8 is plotted in Figure 2-5. The specified delivery rate Q_0 was calculated from the interactive calculator that ALZET® provides (www.alzet.com) and its value is 10.00 µl/hr.

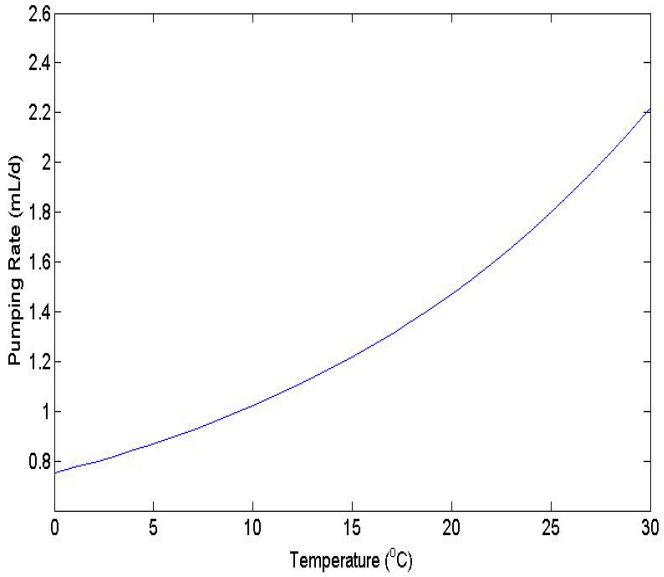


Figure 2-5: Osmotic pump delivery rate and temperature. Calculation based on equation 2-8.

Equation 2-8, was derived from ALZET's® experiments, which for commercial reasons have not been published. This equation applies for a single Alzet osmotic pump, when it operates as a drug delivery system, and it provides the delivery rate of the pump and not the water transport through the outer membrane. Additional parameters that might be affecting the overall delivery rate are:

- the thickness of the layer of the osmotic agent (NaCl) that is placed at the back of the osmotic membrane.
- the behaviour of the elastomeric drug compartment.
- the operation and performance of the of the flow rate moderator and delivery orifice.

Because the flow rate experiments of Alzet® are commercial secrets and the osmotic pumps is an important parameter of this research project, experimental flow rate data are presented in section 3.3.1.

2.2.5 In Situ Osmotically Sampled Continuous Analyser (Nitrate and Iron)

The first application of osmotic pumps in environmental sensors was the submersible osmotically pumped analyser for continuous determination of nitrate in-situ (Jannasch *et al.*, 1994). The basic concept is illustrated in Figure 2-6. Osmotic pumps were used to sample ambient water continuously and to provide the necessary reagents for the nitrate analysis. Standards and blanks are delivered by a microsolenoid pump.

Detection of nitrate is based on an established colorimetric method (Brewer and Riley, 1965), where nitrate is reduced to nitrite on a copper cadmium catalyst, followed by production of an azo dye. The absorbance was measured with an LED (565 nm peak emission)/photodiode detector. The

sampler has low power electronic circuits, which control the operation of the micro – solenoid pumps. The main advantage of the analyser was the low power requirement (less than 35 mW), which can allow for longer deployment periods compared to analysers that use conventional pumps.

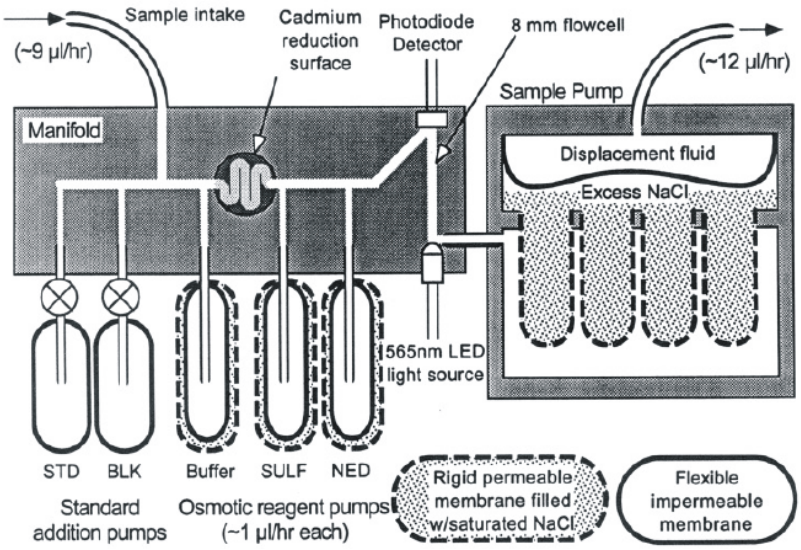


Figure 2-6: Osmotically pumped analyzers for continuous in-situ determination of nitrate. (Jannasch *et al.*, 1994)

The sampler has been tested in controlled conditions, where it performed within expectations. The detection limit was 0.1 µM NO_3^-.

The analyzer's performance was initially evaluated in MBARI's aquarium for a period of one month (see Figure 2-7). The main application of the osmotic nitrate analyzer was in the Bermuda Testbed Mooring (BTM) and in the Hawaii Ocean Time Series (HOTS) moorings, where the analyzer was successfully deployed on a mooring for periods ranging from one to four months. The in-situ Nitrate Analyzer was also used to determine nitrate cycles in an estuary (Chapin *et al.*, 2004).

The same design and engineering approach has been used for an In-Situ total Iron (Fe^{+2}, Fe^{+3}) osmotic analyzer (Chapin *et al.*, 2002). The concept was identical and only the chemistry had changed. The iron osmotic analyzer has been successfully tested both in controlled conditions (MBARI tank) and real aquatic environments. The analyzer was deployed for 6 weeks at 900 m in Monterey Bay, for 8 months on the Loihi Volcano in Hawaii and for 12 months on the Axial Volcano, on the Juan de Fuca Ridge.

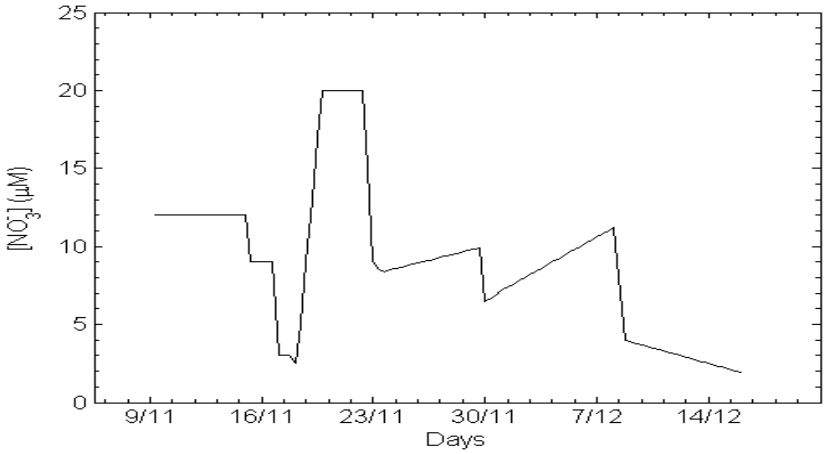


Figure 2-7: Results from nitrate analyzer in MBARI's aquarium. The analyzer was able to capture changes of NO_3^- concentration and responded well to significant concentration differences (figure reproduced from Jannasch et al. (1994)).

The concept of the submersible osmotically pumped analyzer was novel and promising. The osmotic analyzers are more energy efficient than conventional ones (if the term conventional can apply for instruments that are still in an embryonic state), allowing them to operate for a much longer periods of time.

The main disadvantages of these instruments are related to the following issues:

- Delivery of reagents with osmotic pumps is continuous, which does not allow control of the delivery rate and optimisation of chemistry.
- The sampling rate is continuous, but very slow, which increases the response time of the analyser.
- Degradation of reagents and standards during long deployment periods, which leads to drift of the signal and invalid measurements. This issue though is common for all wet chemical analyzers and can be partially mitigated by the use of on board standards and blanks.

Despite these issues, results from both tests and real environment were positive, indicating that for certain applications and for medium term (3-4 months) deployments, these instruments can perform reliably.

Deployments on mooring lines (BTM, HOTS) have stopped and for the last 4 years there have been no publications with data from these analyzers. *Hence the question arises "why" these instruments have not been accepted and utilised by the scientific community?* (A brief answer to this question is given in section 2.5).

2.3 MBARI Osmosampler

2.3.1 Basic Concept

The basic concept of the osmo samplers is illustrated in Figure 2-8. Osmotic pumps or membranes that are used in reverse osmosis (RO) are used to separate a super saturated salt solution (NaCl) and distilled water and create an osmotic gradient, which allows a flow of water from the distilled water compartment to the salt compartment. A long sampling tube, which is also filled with distilled water, is connected to the distilled water compartment. The flow rate through the membranes creates an under-pressure at the sampler's inlet, which allows ambient water to be drawn into the sampling tube. The sample is stored in the sampling tube. The length of the sampling tube is such, that the sample will be retained in the sampling tube during the deployment period and will not enter the distilled water compartment. Usually the sample tube is made from Teflon, which is an inert material and with low friction coefficient (minimum pressure drop). Teflon, however, is permeable to gases, and therefore is not suitable for gas sensitive sampling (e.g oxygen, methane, hydrogen sulphide, carbonate system). If gas sensitive sampling is required copper or titanium spiral tubes can be used.

After the deployment period the sampling tube is segmented and each segment represents a specific time sampling interval. The time/sampling intervals can be adjusted to meet the needs of the survey and the requirements of the analytical methods that will be used.

The main advantage of the OsmoSampler is that it is a very simple and robust instrument, which collects samples continuously without using an electrical power supply, and thus allows for very long deployment periods. The sampler, therefore, can provide chemical time series records with daily resolution. The main drawback of the OsmoSampler is that samples are not physically separated. Hence sampling can be affected by smearing (dispersion), molecular diffusion, bio-fouling and sample degradation. An additional disadvantage is that the flow rate is temperature dependant, so deployments in environments where water temperature varies, will not be constant. All of these aspects are considered in the following sections.

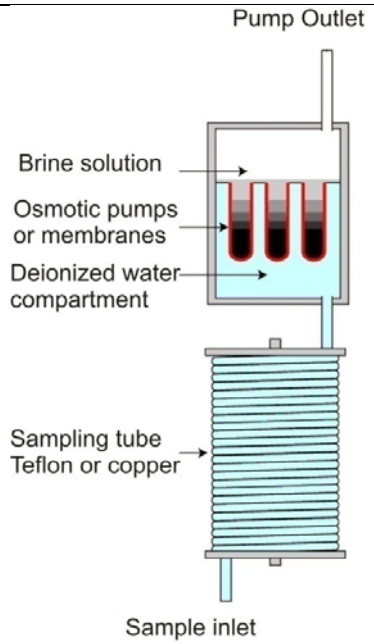


Figure 2-8: Basic concept of osmo sampler.

The technical details (materials and characteristics) of the MBARI osmo sampler are presented in (Jannasch *et al.*, 2004). A critical parameter of the sampler is the pumping rate, which depends, (among other factors e.g temperature, osmotic gradient) on the type and the number of osmotic pumps that are used. The pumping rate can be estimated by multiplying the individual osmotic pump flow rate (section 2.2.4) with the number of pumps that are used. So the total pumping rate is

$$Q_T = Q \cdot n \qquad \textbf{2-9}$$

where Q is the pumping rate of each osmotic pump (equation 2-8) and n is the number of osmotic pumps.

A scientific team in MBARI has designed osmo samplers with pumping rates ranging from 1 to 500 μL/hr. Samplers with twelve osmotic pumps have a pumping rate of 1 ml/d at 20 ^{o}C, while samplers with osmotic membranes, at the same temperature have rates of 12 ml/d.

The flow rate of the osmo samplers is an important feature that has to be determined accurately, as it influences the sample resolution. Flow rates also determine the volume of each sample available for analysis after recovery of the sampler. Consequently, the sample volume largely determines the analytical methods that can be used for chemical analysis.

2.3.2 Sample dispersion & diffusion – theoretical evaluation

Dispersion and molecular diffusion of the samples during the deployment period, is a crucial parameter of the osmo sampler's performance. Hence, in comparing the osmo sampler's features with the requirements of a reliable sampling device (section 1.3.1), the one that the osmotic samplers constructed so far do not clearly meet is that the samples should be discrete and well defined. This is especially true for very long deployment periods, when sample dispersion might lead to false sample identification and or blurring of temporal changes in chemical compositions of the sampled medium.

Jannasch et. al (2004) undertook an extended assessment on the dispersion – diffusion of the sample. In order to study this, they first identified the main processes that can affect sample temporal resolution. These are:

- Molecular diffusion
- Dispersion due to shear forces
- Chemical interactions with tubing walls

2.3.2.1 Molecular Diffusion

The dispersion and diffusion of ions in cylindrical tubes has been studied extensively (Taylor, 1953; Crank, 1956; Bate *et al.*, 1969). The molecular diffusion of solutes in the sampling tube can be calculated from Fick's second law,

$$\frac{\partial C}{\partial t} = D\nabla^2 c \qquad \textbf{2-10}$$

Where ∇^2c is the concentration differentiated in three dimensions, t is time and D is the diffusion coefficient.

For the osmo sampler case, and assuming one dimensional diffusion (small radius of the cylinder), a solution of the above equation is

$$C(x,t) = \frac{C_0}{2} erfc \frac{x}{2\sqrt{Dt}} \qquad \textbf{2-11}$$

where C(x,t) is the concentration of the solute at distance x (cm) from the initial boundary at time t (sec) and D is the ionic diffusion coefficient (cm^2/s) (Li and Gregory, 1974), C_0 is the initial concentration of the solute at $x < 0$. The term erfc is the complementary error function or

$$erfc\, z = 1 - erfz \qquad \text{where} \quad erf\, z = \frac{2}{\pi^{1/2}} \int_0^z e^{-\eta^2} d\eta \qquad \textbf{2-12}$$

Where z is the independent variable and η is an auxiliary variable, which is used only to calculate the integral.

This equation provides the change in concentration of a solute within the sampling tube at different times. The length $2\sqrt{Dt}$ is termed the diffusion length and provides a measure of the longitudinal

diffusion of a substance in time t. Equation 2-11 is plotted in Figure 2-9, where it can be seen that for a one year deployment more than 99% of NO_3^- will remain within approximately 2 m of its initial position in the sampling tube. According to Jannasch et al. (2004) this theoretical approach indicates that, "1 year deployment will exhibit concentration changes with a temporal resolution of 2 days".

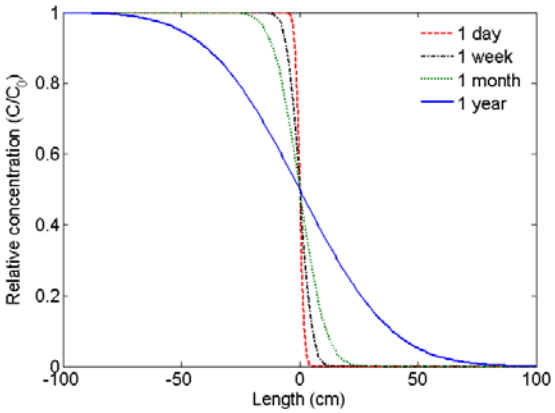


Figure 2-9: Molecular diffusion of NO_3^- in the sampling tube. Each line represents the step change in concentration of NO_3^-, in a small i.d tube after a specific time period. This concentration – distance curve is for an extended source of infinite excess (z = ∞).

Equation 2-11 is derived by integrating the error function over the range [x=0 to ∞]. The diffusion case where a substance initially is confined within a region [-h, +h] is described by equation 2-13 and is plotted in Figure 2-10.

$$C = \frac{C_0}{2}\left\{erf\frac{h-x}{2\sqrt{Dt}} + erf\frac{h+x}{2\sqrt{Dt}}\right\} \qquad \textbf{2-13}$$

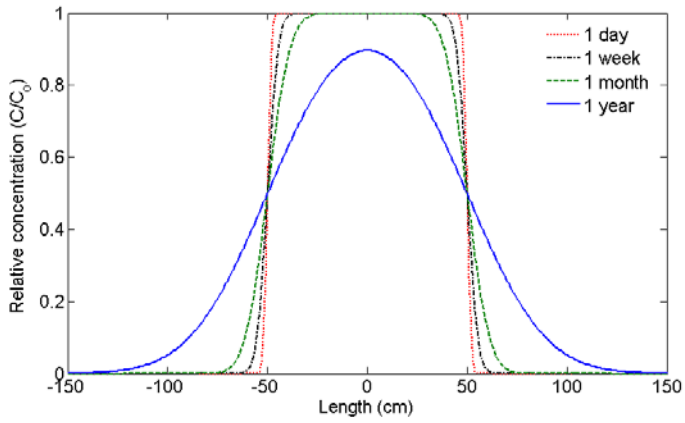


Figure 2-10: Concentration change of a substance limited to [-h, +h] region. Molecular diffusion coefficient $D=1.5\cdot10^{-5}$ cm^2/sec, initial length h = 50 cm (total length = 100 cm, which simulates the length of a daily sample in the osmosampler sampling tube). According to this model the initial length of 100 cm will expand to approximately another 140 cm within a year.

Figure 2-10 illustrates how far the initial strip of the substance will expand with time. It assumes that the molecular diffusion coefficient is constant and that there are no chemical or temperature gradients.

2.3.2.2 Dispersion due to shear forces and interactions with tubing walls

Jannasch et al. (2004) also analyzed the effect of shear dispersion on the assumption that the overall diffusion in the sampling tube is a combined effect of Taylor's effective diffusion (equation 2-14) and molecular diffusion. They came to this conclusion on the basis that Taylor's model suggests that dispersion stops when flow rate stops, which is not realistic. Taylor's model assumes that the axial diffusion can be neglected which causes this inaccuracy. It does however effectively model the effect of radial diffusion that tends to reduce dispersion (see Figure 2-11). Taylor postulates that:

$$k = \frac{r^2 v^2}{48D} \qquad \textbf{2-14}$$

Where k is the "Taylor" diffusion coefficient, r is the diameter of the cylindrical tube, v is the fluid velocity inside the tube and D is the diffusion coefficient of the species in question.

According to the Jannasch analyses (2004), the overall diffusion/dispersion coefficient that best describes the osmo sampler case is:

$$k' = k + D \qquad \textbf{2-15}$$

Substituting in the above equations the values that apply for the osmo samplers (e.g. r = 0.1cm, v = $1.47 \cdot 10^{-3}$ cm/s, D = 10^{-5} – 10^{-6} cm^2/s), it is apparent that the overall diffusion coefficient k' is very similar to D. This analysis is illustrated in Figure 2-11. It is clear that in this geometry, radial diffusion reduces dispersion more effectively than axial dispersion increases it. Therefore the greatest dispersion is observed if diffusion is neglected (sheer only dispersion).

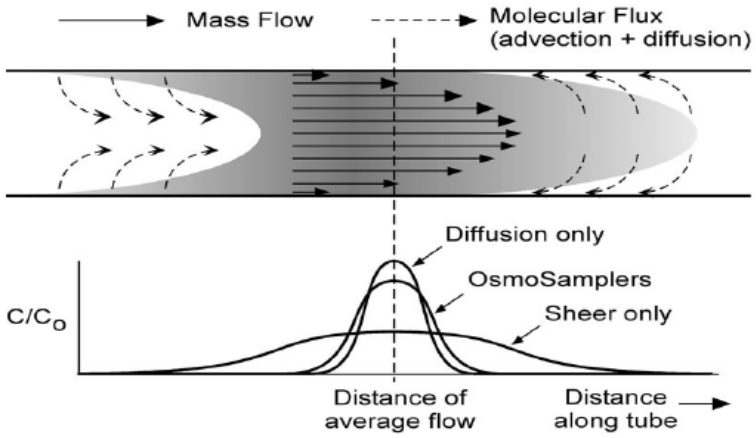


Figure 2-11: Dispersion of solutes in the sampling tube of an osmo sampler. (Jannasch *et al.*, 2004).

Sample integrity may also be affected by "chromatographic" behaviour of solutes with the sampling tube surfaces. This will happen if the solutes have a chemical affinity with the tubing material and attach to the tubing wall. To minimize this effect, the sampling tube is from chemically inert materials (e.g. Polyaryletheretherketone (PEEK), Teflon).

Theoretical determination of dispersion and diffusion is crucial in order to predict the sampler's performance, but experimental evaluation and field tests are necessary, in order to ground truth the theoretical predictions. Results from laboratory experiments and field applications of osmotic samplers are presented in section 2.3.3.

2.3.3 Performance of OsmoSamplers

As stated above, determination of the dispersion of solutes in the sampling tube is a very important aspect of OsmoSamplers. It is necessary to examine these processes during operation of the osmo sampler and to realistically quantify them. Jannasch et al. (2004) evaluated sample dispersion by monitoring the flow rate and altering the inlet sample (seawater to distilled water to altered seawater), in order to get distinctive differences in concentration during sampling. The experiment lasted for two months. The results from their study indicated that for a 2 month deployment the performance of the OsmoSampler in the laboratory was reliable (changes - boundaries in concentrations were integrated within a 1.5 day subsample). The next step was to deploy the sampler in natural marine environments.

Over the last 10 years OsmoSamplers have been used in a number of projects. Applications include boreholes (Morris *et al.*, 2003), hydrothermal vents (Kastner *et al.*, 2000; Jannasch *et al.*, 2004) and marine gas hydrate fields (Carson *et al.*, 2003). Deployment periods ranged from several weeks up to 4 years and deployment depths were from surface waters to 5000 m. Submersibles and remotely operated vehicles (ROVs) were necessary in a number of these deployments.

Overall the performance of OsmoSamplers was encouraging and promising. In most of the long term deployments, the samplers managed to capture changes in seawater and porewater chemistry. Data from Osmosamplers prove that changes in water chemistry can be captured with osmo samplers and resolution can be retained, dispelling the fears of a homogenized sample due to molecular diffusion and smearing of sample. One example is illustrated in Figure 2-12, where discrete changes in concentrations of Fe, Sr and Ba, at a hydrothermal vent site, are visible.

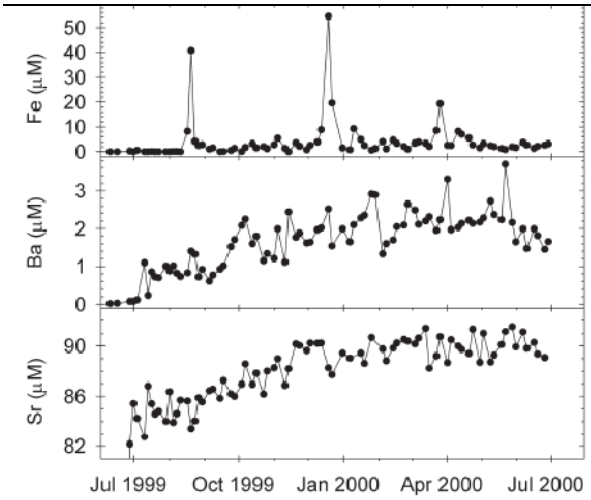


Figure 2-12: A year long record of OsmoSamplers from "Marker 33" vent. Results indicate the ability of osmo samplers to retain temporal resolution and capture changes in water chemistry (Jannasch *et al.*, 2004).

Results from OsmoSamplers were compared with results from discrete samples (Wheat *et al.*, 2000; Wheat *et al.*, 2003; Jannasch *et al.*, 2004), which were sampled by conventional means. This comparison showed similar results, producing further evidence of the OsmoSamplers reliability.

Most of the OsmoSamplers deployments were inside boreholes, sampling porewaters from sediments. In some deployments OsmoSamplers were re-designed to meet the needs of the environment; therefore, the design was very thin and long. In some OsmoSamplers an acid addition (HCl) device was incorporated, to keep trace metals in solution and preserve the sample. The acid was delivered with an osmotic pump configuration that was designed to deliver an acid to sample ratio of 1:20. Comparison between standard and acid addition samplers indicates the necessity of preservative for reliable determination of redox sensitive elements. The acid addition concept can be adapted to the sampling and analytical requirement, so that different preservatives can be used in different settings.

Another issue that influences the performance of osmotic samplers is penetration of suspended matter in the sampling tube, which can block the sampling tube and compromise sampling. In most deployments such problems were not reported. An example that illustrates this problem has been reported during deployment of OsmoSamplers to collect hydrothermal fluids from Loihi Seamount (Wheat *et al.*, 2000). After recovery of the OsmoSamplers it was found that two of them had clogged sampling tubes. The fluid in the sampling tube was found to be a homogenized mixture of deionized water and seawater. The sampling tubes were clogged from iron oxide sheaths that are biological in origin.

2.4 Alternative marine applications of osmotic pumps and osmo samplers

The simple nature of osmotic pumps and the successful deployments of osmotic samplers, gave researchers and engineers the confidence to develop new instruments based on osmotic pumps. Two of such instruments are described below.

2.4.1.1 OsmoFlow meter

An instrument that is very similar to the osmo sampler is the OsmoFlow meter (Figure 2-13) that was also developed in MBARI. OsmoFlowmeters were deployed in boreholes (Integrated Ocean Drilling Program (IODP) 1253A and 1255A (Morris *et al.*, 2003)) to monitor the flow rate of porewaters and direction of the fluids within the borehole. OsmoFlowmeters use the discharge of OsmoSamplers to inject tracers into the pore fluid at a constant rate. The tracer is carried by the porewaters and enters the instrument via the perforated and wired wrapped casing. The injection rate of the tracer is the same as the pumping rate of the osmo sampler so that the sampling – injection rate can be easily deduced. The porewater/tracer mixed liquid is sampled by osmo samplers that are placed in each of four directions. The pore water direction and flow rate is then deduced by the differences of the tracer concentration in each osmo sampler's subsample.

In the IODP deployments, the OsmoFlow meters were attached to a CORK (Circulation Obviation Retrofit Kit). The CORK is a system to seal a reentry hole after drilling. It is equipped with sensors and instruments that sample and monitor the hole (including OsmoSamplers and OsmoFlowmeters) while the system recovers from the drilling and returns to equilibrium.

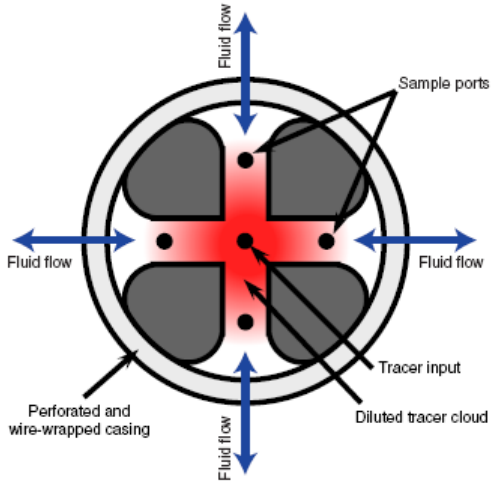


Figure 2-13: Cross section of OsmoFlowmeter. OsmoFlowmeters were deployed in holes 1253A and 1255 A under IODP (Morris *et al.*, 2003).

Through applications of this technique, OsmoFlow meters are able to detect flow rates of less than 1 ml/d to more than 4 L/day (Carson *et al.*, 2003). In addition, porewater flow rate data, when combined with chemical analyses of the stored pore fluids, yields fluxes of chemicals between the sea floor and the oceans.

The OsmoFlow meter performance was encouraging, and the main challenges were associated with the CORK system. The main problem is that the CORK system is a rather "turbulent" and disruptive way to sample pore waters. This is because drilling the borehole, in order to deploy the CORK system, disturbs the thermodynamic and geochemical equilibrium between the sediments/bedrock and the pore waters. According to the designers and users, these systems are still in an embryonic state, and further development is necessary in order to tackle challenges.

It is worth noting that at ODP site 892B (Carson *et al.*, 2003), osmo samplers were used to sample pore waters that were also analyzed for microbiological parameters, such as phylogenetic – taxonomic classification of bacteria. According to Carson et al. (2003), the osmo samplers gave microbiologists the chance to study these parameters over a long period in these environments, which are otherwise very difficult to access and sample. Results were very encouraging and reliable. This new application of osmotic samplers further expands their application horizon, and may provide the opportunity for osmo samplers to become more widely accepted by the oceanographic and environmental scientific community.

2.4.1.2 Multiple Orifice Sampler and Quantitative Injection Tracer Observer (MOSQUITO)

The MOSQUITO (Solomon *et al.*, 2008) has the same concept as the OsmoFlowmeter, and has been deployed in gas hydrate fields to sample fluids and gases from the hydrates. The MOSQUITO is equipped with osmo samplers which have a titanium tube attached to their inlet. The probe is immersed into the sediment at the desired pore water sampling depth. Multiple osmo samplers are used to sample pore waters from various sediment depths and in various flow directions. The MOSQUITO, like the OsmoFlowmeter, also has a tracer injection system. The tracer is injected into the sediment via a titanium probe, mixes with the pore water and is sampled along with the pore water flow by the osmo samplers. Flow rates, direction of pore waters and chemical fluxes can be deduced by the tracer and chemical species concentration. The main advantage of the MOSQUITO compared to the OsmoFlow meter is that the sampling method does not require a borehole. Therefore the *in situ* thermodynamic and geodynamic equilibrium is not so heavily disturbed during sampling. As can be seen from Figure 2-14 the whole device is placed at the sediment surface and submersibles or ROVs are then used to insert the titanium probes into the sediment.

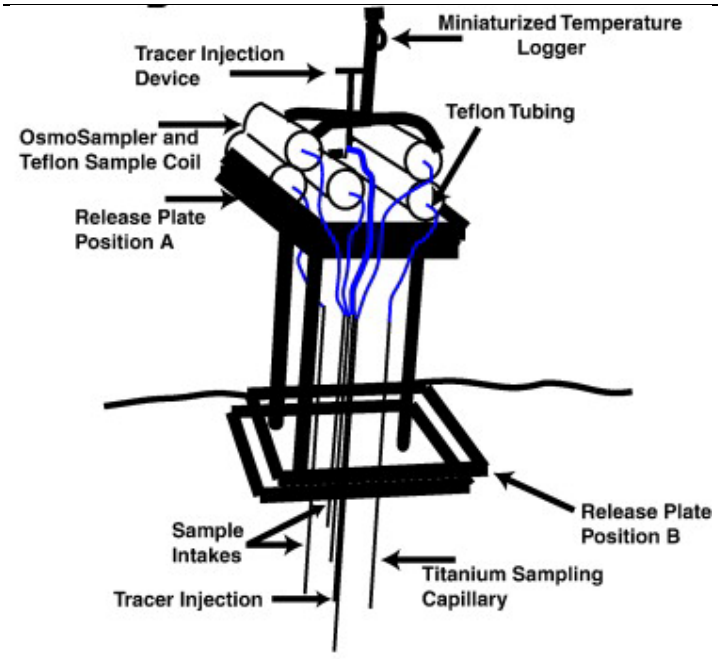


Figure 2-14: Sediment fluids (porewaters and gas hydrates) sampling device; MOSQUITO (Solomon *et al.*, 2008).

MOSQUITOS were tested both in the lab and in real conditions and they have been evaluated against Peepers and Push cores (porewater extraction from cores in the lab) that are established techniques for porewater sampling.

Results from the deployment of four MOSQUITOS in the northern Gulf of Mexico (Bush Hill, (Solomon *et al.*, 2008)) helped to identify gas hydrate formation and revealed frequent changes in the subsurface hydrology. These results revealed both upward and downward water fluxes (-161 to 273 cm/yr) and changes in chemistry that coincide with gas formation (Cl^- maxima at 590 mM during high flow rates of 273 cm/yr). This application of the MOSQUITO was the first long term deployment (~ 430 days), during which all the instruments performed well and operated within expectations. Coupling of the osmo samplers with pressure and temperature sensors and the injection of a tracer provides a complete package for porewater sampling and monitoring. The successful deployments of such instruments will allow them to be improved and will provide scientists with the means to study similar processes in the environment.

2.5 Discussion on Osmo samplers and Osmo - applications

Since 1994 osmo instruments have become part of the arsenal used to observe aquatic environments. The main advantage of these devices is that they pump fluids for a long period of time without using electrical power. As many monitoring and sampling programs are in remote and very difficult to access sites, this feature is highly appreciated. Another important advantage of

such samplers is that the manufacturing cost is low. They do not have any moving or mechanical parts, so they are also robust and easy to maintain.

The main drawback of these instruments is that pumping rate is continuous and cannot be controlled. As a result samples are not discrete, interact continuously and sample identification is not easily defined. Despite these challenges, osmo instruments can facilitate research that would have been impossible with conventional pumps and samplers.

Osmo analyzers were the first platforms to use "osmo power". These instruments have proven themselves in deployments on time series moorings (BATS, BTM, HOTS) but they still have not been used extensively, even though they have significant advantages (long term deployments, high sampling resolution) and the data are reliable. The reason why these instruments have not been adopted by marine chemists and geochemists is, probably, that they are not commercially available and have not been marketed to the sensors – instruments market. Therefore the most common way of using such instruments has been to collaborate with the scientific teams that developed and used them, or for the interested party to develop them from scratch (see section 2.2.5).

Collaboration is always desired, but as these analyzers are not commercially available, they are few in numbers and can only facilitate a small number of projects. "Development from scratch", is also difficult as not all research institutes and marine centres have the necessary means to develop instruments.

OsmoSamplers are the most common and widely used instruments that use "osmo power" to replace conventional pumping equipment. OsmoSamplers are very versatile, can facilitate various scientific needs as they are very simple to manufacture and to use. The collected water samples can be analyzed for most inorganic species, but the small sample volumes can limit the analytical opportunities, as solutes with very low concentrations might be difficult to analyze. The advance, however, of analytical techniques and their ability to detect very low concentrations with small sample volumes, will aid the sampler's improvement.

The fact that IODP includes OsmoSamplers in their projects is an indication of their growing acceptance. It is surprising, however, that there have been very few deployments in coastal environments, rivers and estuaries (Golshani, 1998), given that osmotic samplers can be suitable for monitoring and sampling projects in such environments. As stated in chapter 1, the dynamic and constantly changing nature of these aquatic environments, requires long term, autonomous sampling and monitoring systems, in order to capture and measure these changes.

Based on this concept we have designed an osmo sampler, which can be more useful for mid to long term deployments in terrestrial and coastal marine environments.

3 Southampton Continuous Autonomous Water Sampler (SCAWS)

3.1 Rationale and Design concept

The design concept of the SCAWS is similar to the OsmoSamplers that have been described in the previous chapter. The basic issues that influenced the design parameters of the SCAWS were the s*ampling/flow rate range*, the *desired deployment period* and the desired *research/chemistry outcome*

However the design is optimised for deployment in a wider range of environments. Applications for the SCAWS are anticipated to be rivers, estuaries and sea surface, where physical, biological and geochemical characteristic are different than those in benthic marine environments, where osmosamplers have largely been deployed in previous studies. Two parameters that are particularly important in affecting the operation of the osmo sampler are:

- Temperature
- Suspended solids concentration

3.1.1 Temperature

The relationship between osmo sampler pumping rate and ambient temperature was described in section 2.2.4. It is evident that without compensation, variation in the pumping rate determines the precision with which the age of the sample is known as a function of the sampling tube length and consequently the scientific outcome of the sampling. As mentioned in the previous chapter, most of the deployments of osmo samplers were in deep benthic environments, where temperature is constant and therefore the pumping rate is constant. With this assumption, segmenting the sampling tube at predetermined lengths should not yield large errors in terms of the temporal assignment of the samples.

However, in surface waters temperature can vary significantly between seasons (seasonal changes: hot – cool season) and in some cases within days (diurnal: night – day variations). Consequently the pumping rate of osmo samplers will vary. Therefore if the sampling tube is segmented at predetermined lengths, the age of each sample will not be accurately determined. Hence it is necessary to have a mechanism that will solve this problem. One option is to record the temperature and deduce the pumping rate from the pumping rate – temperature relationship, discussed in section 2.2.4. A temperature sensor and a data logger are required, but if these fail, it will still be difficult to segment the tube accurately into well – constrained time intervals.

3.1.2 Suspended Solids

Suspended solid concentrations are variable in surface waters. For example high concentrations of suspended sediments are expected in river waters during wet seasons when flow rates are high. During spring and summer, the increase of biological activity (phytoplankton blooms) will also lead to higher concentration of suspended matter in marine surface waters. During such conditions biofouling of monitoring instruments and equipment may be severe and failure of their operation is possible. Chapter 2 includes evidence that even in environments with relatively low suspended load concentration some of the OsmoSamplers failed because the sampling tube became blocked by solids that entered the sampling tube.

3.1.3 Design Concept

It is therefore essential to find solutions to these challenges. The potential solutions considered here are:

- Time stamp the sampling tube with a tracer.
- Install a filtering device to prevent suspended matter entering the sampling tube.

The main concern with both of these approaches is that these features may render osmo samplers less robust and more complex. Moreover, these features require electrical power to operate them, which may reduce the effective deployment period of osmo samplers. Nevertheless, if the concerns are not addressed, deployment of osmo samplers in surface waters may not yield representative samples and accurate data. Therefore, in solving these problems it is important for the new devices to be as simple and robust as possible. In addition, the design should also consider the manufacturing cost of the sampler and try to produce an instrument with as low a cost as possible. The design and testing of the SCAWS's components are described in the following sections.

The operational concept of the SCAWS is presented in Figure 3-1.

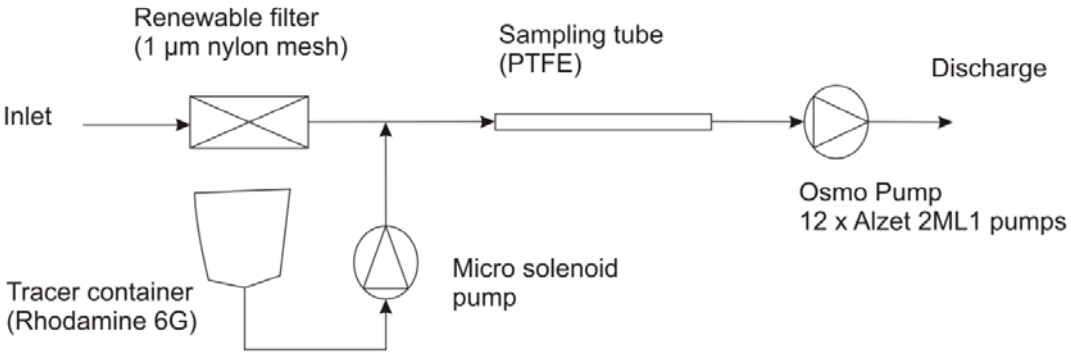


Figure 3-1: SCAWS fluidics diagram.

3.2 Design of the SCAWS

3.2.1 Osmo Pump Design

One of the most important aspects of the osmo pump is the pumping rate. The pumping rate depends on the number of osmotic pumps, which constrains the physical dimensions of the osmo pump. For the SCAWS the desired sampling rate is 1 – 2 ml/d, because the resultant volume of a daily sample is then sufficient for analyses of the most important analytes and dispersion and diffusion will remain at low levels. For this desired pumping rate and with temperature ranging from 5 – 30 ^{o}C, (equation 2-8), it is calculated that twelve ALZET 2ML-1 osmotic pumps will cover these requirements.

With such slow flow rates inside the sampling tube, the flow rate is laminar and the velocity profile is parabolic and the pressure drop across the sampling tube, due to friction does not affect the operation of the pump (see section 3.2.2 for pressure drop calculation).

The osmotic pump is cylindrical in (Figure 3-2), with 120 mm diameter and 118 mm length. The basic parts of the osmo pump are described below:

- *Salt water – Deionized water compartments.* The volume of the salt water reservoir is ~ 316 ml. Commercial grade NaCl (Fischer Scientific) was used for the brine solution. The amount of NaCl that is added is not critical as long as the solution remains supersaturated throughout the deployment, thus maintaining a constant osmotic gradient. A 60:40 salt to water ratio was sufficient to maintain a supersaturated brine solution for more than one year (December 2005 – August 2006). Even after that period, a substantial amount of salt crystals were visible indicating therefore, that with this amount of salt it is possible to sample continuously for more than a year. The deionized water compartment is ~ 410 ml (slightly bigger than the salt water one, because it has to fit the length of the osmotic pumps).
- *Holding plate for Alzet Osmotic pumps and retainer*: Twelve osmotic pumps– Alzet 2ML1 model – are placed in the middle plate and secured with a retaining plate. Viton o-rings are placed on the upper part of the osmotic pumps, which are pressed by the retainer and provide a seal for the osmotic pumps. The osmotic pump inner drug compartment was removed so that water flow is not restricted. The pumps are aligned in two circular arrays (nine on the outer circle and three on the inner one). With such an alignment, dimensions are minimized and there is enough space between the pumps for it to be easy to mount them on the plate. The holding plate and the retainer are attached with stainless steel bolts. Stainless steel bolts are better than plastic ones as they can be fixed tighter and they do not absorb water. The stainless steel bolts are located in the deionized water compartment so

that they do not corrode. Contamination of the sample with metals is not possible, because the bolts do not make contact with the samples.

Except where indicated, the above parts are made from polymethyl methacrylate (trade name Perspex). Perspex was chosen because it is easy to machine, inert to many inorganic chemicals, it is transparent (so it is easy to check if there is something wrong inside the two compartments) and it has very low water absorption. Moreover, Perspex has a similar thermal volumetric expansion coefficient to water, which means that volumetric changes of water and Perspex, due to temperature differentiations, will be similar. This minimizes rapid modulation of the pumping rate due to differential expansion.

Detailed drawings of these parts are presented in the APPENDIX.

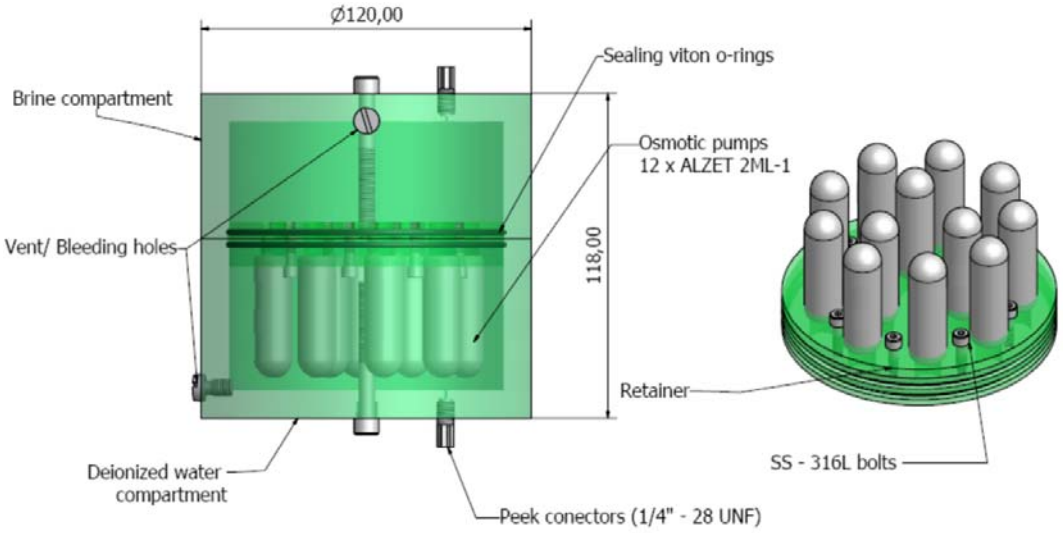


Figure 3-2: Osmo pump for the SCAWS. Dimensions are in mm.

3.2.2 Sampling/storage tube & Spool

The sampling/storage tube is a 1mm internal diameter Fluorinated Ethylene Propylene (FEP/Teflon) tube. Teflon is a recommended sampling material for most inorganic and organic analytes, because it is resistant to strong acids, enabling it to be cleaned and used for trace metals sampling. It also has low friction coefficient, which will reduce pressure drop losses. Teflon tubes are transparent so any blockages are visible. The only disadvantage, of Teflon, is that it has relatively high gas permeability, so it cannot be used to sample dissolved gases in water.

The length of the sampling tube depends on the deployment period and the temperature of the environment. An example for the calculation of the sampling tube is presented below:

Deployment period = 180 days

Maximum temperature = 15 ^{o}C

Pumping rate = 1.2 ml/d (equation 2-8)

Maximum volume (MV) = 180 d x 1.2 ml/d = 216 ml

Specific Volume of 1 m sampling tube (SV) = Cross section area (cm^2) x Length (cm) =

$$\pi \cdot \frac{d^2}{4} \times L = 0.00785\ cm^2 \times 100\ cm = 0.785\ cm^3$$

$$\text{Total Length} = \frac{MV}{SV} = \frac{216\ (cm^3)}{0.785\ (cm^3/m)} = 275\ m$$

Safety factor = 20% (Maximum error of the flow rate of osmotic pumps see section 3.3.1)

Final Sampling tube length = 303 m

The pressure drop along the tube must be calculated to check that the osmo pump operation is not compromised. Pressure drop is calculated using the D'Arcy – Weisbach equation 3-1.

$$\Delta p = \lambda \cdot \frac{L}{d} \cdot \left(\frac{\rho \cdot u^2}{2}\right) \quad \textbf{3-1}$$

$$\lambda = \frac{64}{Re} \quad \textbf{3-2}$$

$$Re = \frac{u \cdot d}{v} \quad \textbf{3-3}$$

Where:

Δp = Pressure loss (Pa or $N/(m^2)$)

λ = Friction coefficient which is calculated from equations 3-2 and 3-3

Re = Reynolds number

L = tube length (m)

d = Tube diameter (m)

ρ = Density of fluid (kg/m^3)

u = velocity of fluid in the sampling tube (m/s)

v = kinematic viscosity (m^2/s)

For a sampling tube of d = 1mm internal diameter, L = 300 m length, where water flows (density = 999 kg/m^3) with a velocity of 1 ml/d (1.18×10^{-5} m/s) the pressure drop is 1700 Pa (0.017 bar). The osmotic/pressure gradient generated by the osmo pump and is calculated from equation 2-1. According to this equation and with a 60:40 (w/w) NaCl solution, at 23 ^oC, the osmotic pressure generated is 253 bar.

The sampling tube is connected to the rest of the components with zero dead volume connectors (Omnifit or Upchurch). All connectors are made from polyaryletheretherketone (PEEK), which is

inert, easy to clean, durable and not susceptible to biofouling. The sampling tube is coiled on a spool (see drawings). The spool is made from black acrylonitrile butadiene styrene plastic (ABS).

3.2.3 Tracer addition – Time stamping

The rationale behind the use of a tracer addition system was noted in section 3.1. The basic concept of the system is to "trap" the sample between two tracer additions as is illustrated in Figure 3-3. The ideal tracer for this application should have the following characteristics:

- Inert and does not contaminate the samples
- Diffusion coefficients should be as low as possible, so that the injections are discrete and do not mix with each other
- The two injections should be visually distinguishable (vibrant colour) so sample segmentation is easier.
- Environmental friendly, so in case the tracer's container is damaged the aquatic environment is not polluted.

Fluorescent dyes, like fluorescein and rhodamine can be used as markers, and are used widely in groundwater hydrogeology for the identification of underground water paths (Kasnavia *et al.*, 1999; Sabatini, 2000; Smart and Karunaratne, 2002).

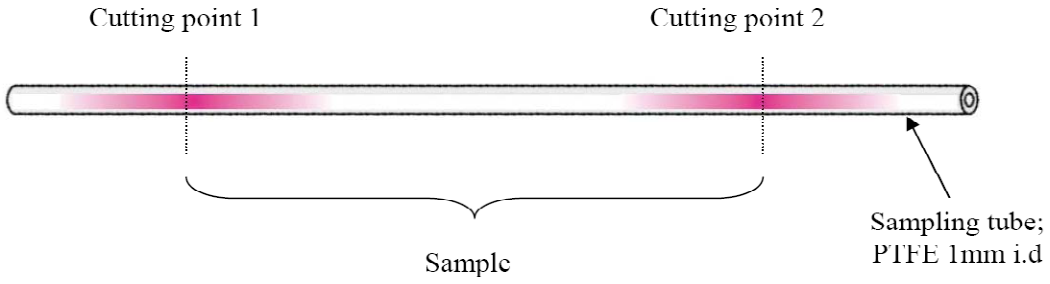


Figure 3-3: Basic concept of the tracer addition system.

For the SCAWS water solutions of fluorescein and rhodamine 6G were used, which were stored in collapsible blood bags (Baxter Co.). The exact concentration of the solution is not important as the purpose is to detect the rhodamine strip visually, before cutting the sampling tube. After the initial tests rhodamine 6G was chosen, mainly due to its ability to retain a more vibrant color after longer periods than fluorescein. This is mainly due to the higher photostability of rhodamine 6G, compared to fluorescein. Moreover, rhodamine water solutions are stable in acidic conditions, while fluorescein loses its fluorescent properties. This feature was considered important in case it was decided to add acid (e.g. HCl) to preserve the samples. However it should be mentioned that the rhodamine we used contaminates the samples with chloride, sodium and sulphate by 0.1 mM, 0.05 mM and 0.02 mM respectively. This was found after the river water deployments. Because

such contamination is significant, the use of rhodamine 6G for river water applications, needs to be reconsidered (see chapter 7, Future Plans).

The tracer is injected into the sampling tube using a solenoid micropump (Lee Co. Ltd). The characteristics of the pump are:

Model:	LPLA1210550L
Dispensing volume:	50 µl
Accuracy:	± 5 %
Voltage:	12 V DC
Current draw:	200 mA
Power requirement:	2 W
Tube connections:	Lee minstac connectors

The outlet of the solenoid pump is connected to the sampling tube with a PEEK T-piece (Omnifit). The tracer initial injection is directed towards the inlet of the osmo sampler's tube; the sample tube and osmotic pump chamber has low compressibility whereas there is a low resistance path to the open ended inlet. The 50 µl of tracer occupies approximately 6 cm of the sampling tube, so the T-piece is installed 10 – 15 cm after the inlet of the osmo sampler, to prevent loss of the tracer.

The solenoid pump is placed in a water proof container (Figure 3-4) made from white polyoxymethylene plastic (trade name Acetal/Delrin). The same size Teflon tubing and same PEEK connectors are used to connect the rhodamine store (blood bag) and the sampling tube (T-piece) with the container and the pump. Power supply is provided by a water and pressure proof electrical connector (Bennex® Micro-Wetcon). One end of the case is sealed with an expandable rubber membrane, which can act as a pressure compensating device, when the case is deployed in deep (>10 m) environments.

The micro-solenoid pump is controlled by a custom made electronic circuit (see section 3.2.5).

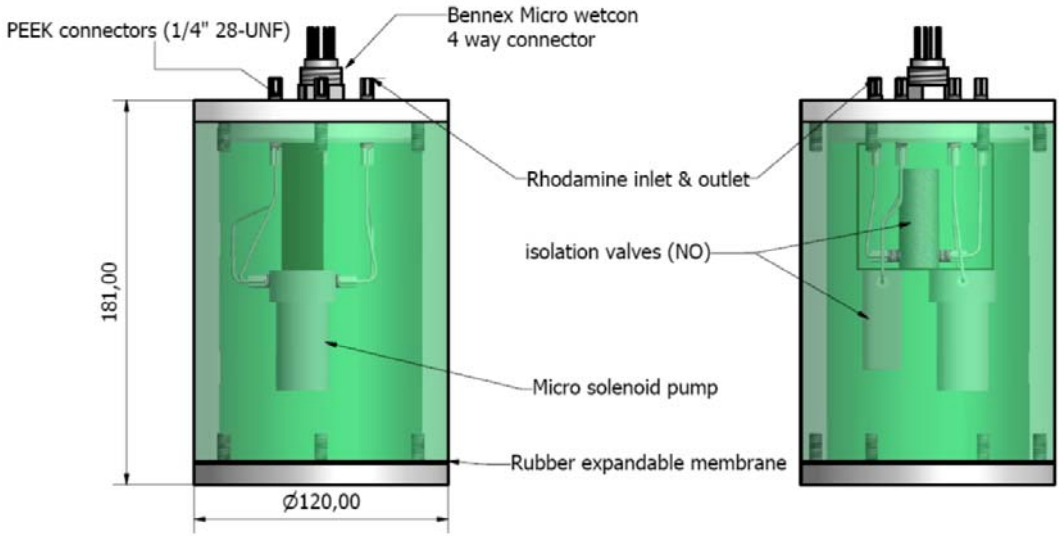


Figure 3-4: Case for micro solenoid pump – tracer addition. The isolation valves are normally open valves (NO). The main purpose is to close the valves before recovering the instrument, so that the samples inside the tube are not affected by pressure changes. Isolation valves were not included in the first prototypes.

3.2.4 Filtering system

The design of the filtering system focused on the following issues:

- Effective filtration of the sample
- Periodic renewal of the filtering media so that it does not become blocked or fouled
- Small physical dimensions
- Power efficient

Considering the above, it was decided to design a filtering device that is similar to a cassette tape or a cassette for photo films (Figure 3-5). The design enables renewal of the filtering medium with small power requirements. The cassette filter is comprised of several parts, which are connected with nylon or stainless steel screws. The filtering medium is a 1 μm nylon mesh (SEFAR). The filter comes in sheet rolls and then it is cut in 12 x 1,600 mm strips. The strips are washed thoroughly with deionized water, ultrasonicated, washed again with deionized water, dried in a laminar flow hood and then placed in the cassette filter. Acid cannot be used as it will dissolve the nylon mesh. When trace metal clean sampling is required, Teflon meshes are available, but they are more expensive.

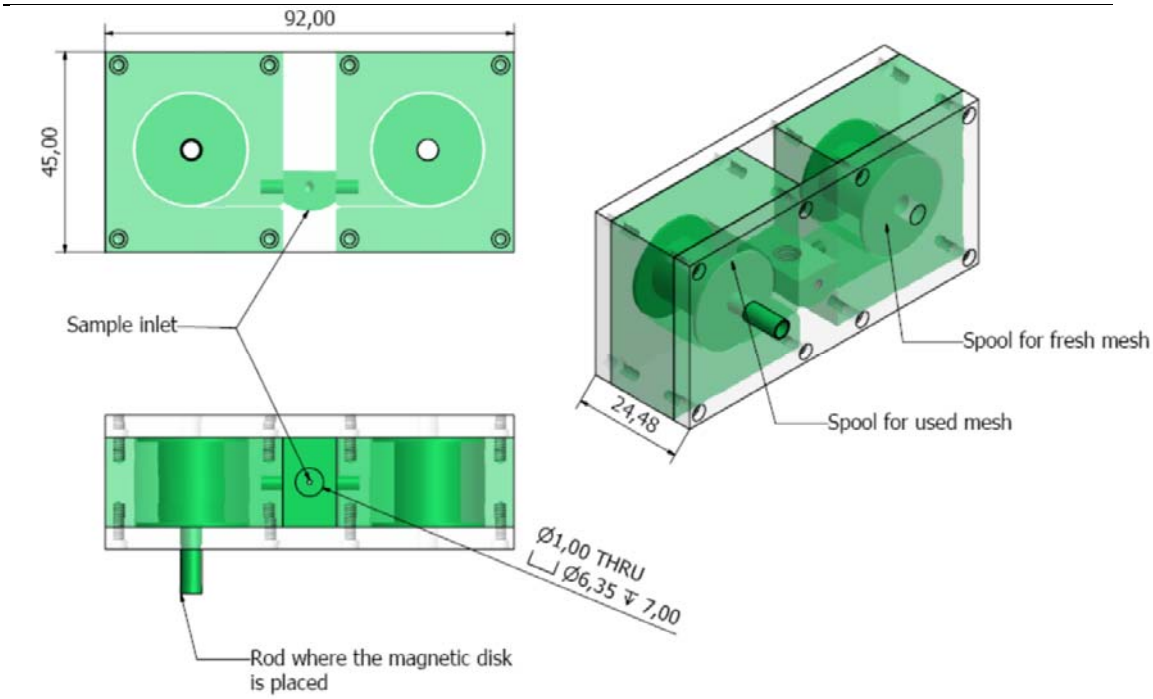


Figure 3-5: SCAWS's filtering device.

For long deployments it is important to renew the exposed nylon mesh, otherwise it is possible that the mesh will become clogged and pumping will be distorted, or even stopped. Fouling could also alter the sample as it passes through the filter. To achieve filter renewal one of the cassette's spools is connected on a stepper motor, via an axial attractive magnetic coupling. The magnetic coupling allows the stepper motor to be enclosed in a waterproof box and secured, but still able to transfer power to the cassette filter. The stepper motor has attached gears, which allow more efficient operation of the system (calculations are presented in the APPENDIX). The characteristics of the stepper motor are:

Model:	McLennan P542-M48U1
Motor type:	Unipolar
Gear ratio:	25:6
Rated voltage:	5 V
Current per phase:	550 mA
Max working torque:	13.5 Ncm

The magnets are cylindrical rare earth magnets (REM), which are placed in plastic (black Delrin) cylindrical plates. The connection of the stepper motor box and the cassette filter is illustrated in Figure 3-6. It is important to note that the connection has to be very precise, because any misalignments will increase the friction between the cassette filter magnet and the stepper motor box lid and disrupt the renewal of the mesh.

We used magnets of two sizes, in different configurations (Figure 3-7). Experiments in the laboratory with the different coupling configurations indicated that for the SCAWS the most efficient configuration was with two 12x5 mm REM magnets.

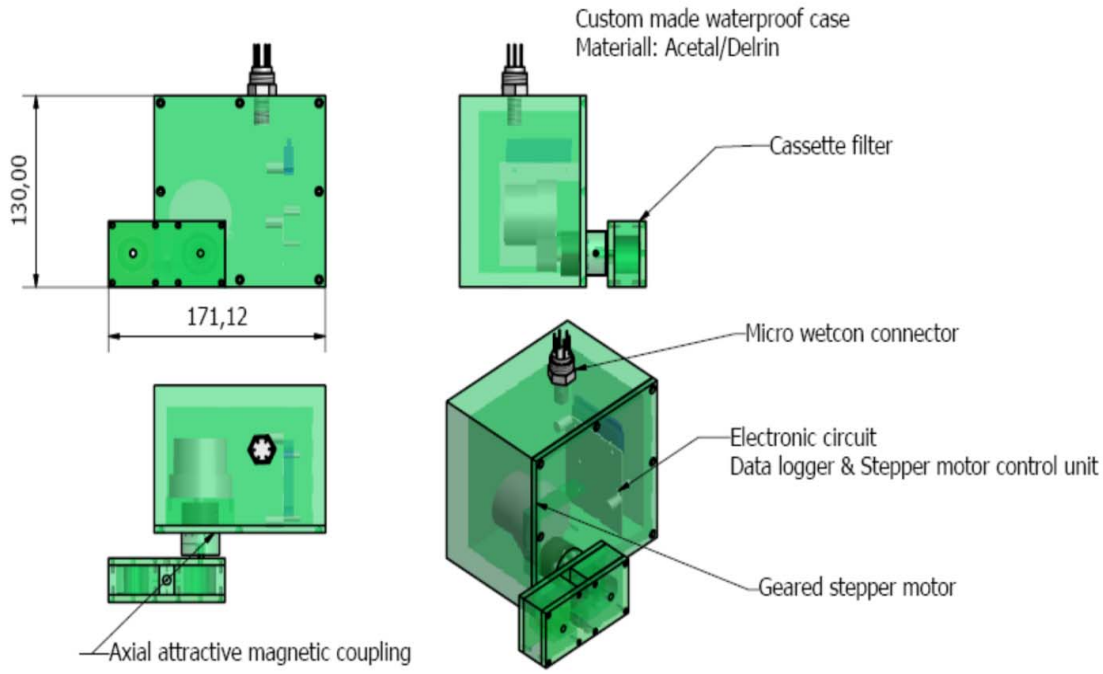


Figure 3-6: Cassette filter and stepper motor (Dimensions are in mm).

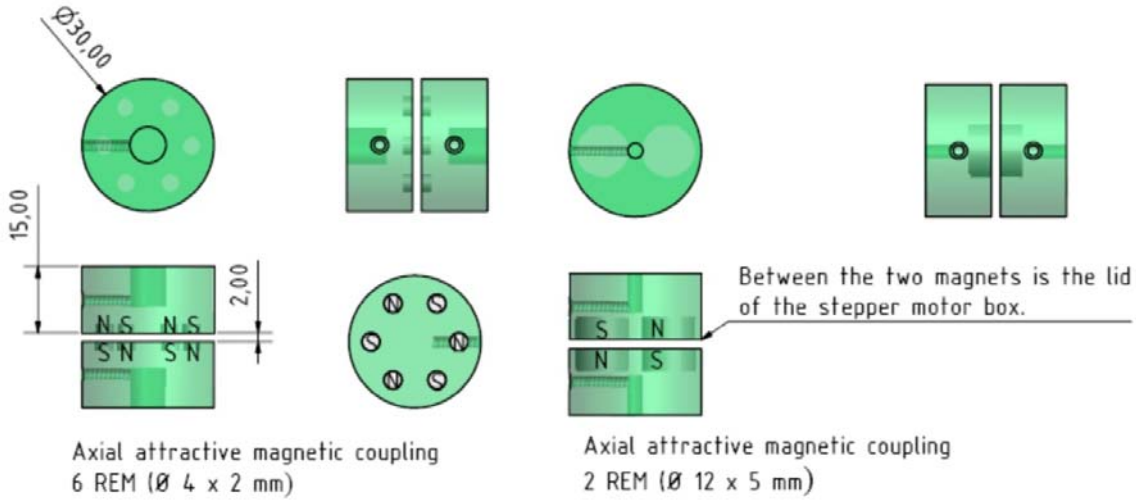


Figure 3-7: Alignment of the axial magnetic coupling. (Dimensions are in mm; REM: Rare Earth magnets).

3.2.5 Electronic Circuit

Both the solenoid micro pump and the stepper motor are controlled by an electronic circuit. The main part of the electronic circuit is a custom made Data Logger designed in NOCS – NMFD. In addition to the Data Logger it was necessary, to design an electronic circuit to control the stepper motor. The basic concept of the operation of the electronic circuit is presented in Figure 3-8. Detailed circuit diagrams of both electronic circuits are presented in the APPENDIX.

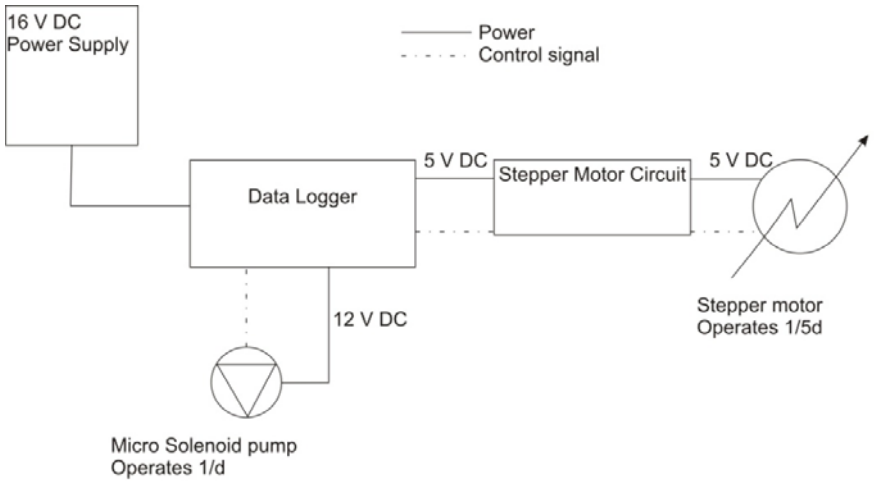


Figure 3-8: Basic concept of the electronic circuit operation.

The main part of the data logger is a PIC Microcontroller, which controls the operation of the pump and motor. The PIC was programmed in C language (see APPENDIX for code). The data logger real time clock can be programmed to operate both devices at intervals between 1 second and 2 weeks. The basic component of the stepper motor circuit is the motor driver chip, which receives a square wave signal from the PIC and operates the stepper motor. For the SCAWS it was decided to operate the pump once a day (1 pulse delivers 50 μl) and the stepper motor every 5 days. This means that once a day, for approximately 1s, the current consumption will be 200 mA (pump), and once every five days the current consumption will be increased by 500 mA for another 10s (stepper motor operation). During the rest of the deployment period the electronic circuit should not consume any power if possible. For this reason all the parts of the data logger that are not used were deactivated. The power consumption of the electronic circuit – while in this standby mode – was reduced to 0.8 – 1.6 mW. Considering that the electronic circuit is powered by a 15.6 V battery pack (12 AA x 1.3 V rechargeable batteries), with 2100 mAh current capacity, it is estimated that this battery pack can sustain the operation of the sampler for approximately 60 days. Larger battery packs are available, should longer deployments be necessary.

3.2.6 Complete Sampler

Two prototype samplers were developed. The first was a non – autonomous version, which required electrical power from external sources. The Mark I (MK I) prototype is presented in Figure 3-9.

The MK I was used for initial tests in order to evaluate the performance of the sampler. The main priority was to establish that the osmo pump can operate in natural aquatic environments. At the same time, it was necessary to test the performance of the tracer addition scheme and the ability of the filter renewal mechanism to operate in natural environments.

The first autonomous SCAWS prototype (MK II) was ready in December 2007. The complete sketch for the MK II prototype is shown in Figure 3-10.

The actual outcome is presented in Figure 3-11. Minor differences between the cartoon (Figure 3-10) and the actual product have to do with the cover of the sampler, as it was more convenient to modify and use a plastic tube that was already available in NOCS workshops.

The MK II sampler was deployed twice in a local river; the first time for a period of one week and the second time for a period of one month (see sections 6.2 and 6.3).

Both of the prototypes are larger than would have been ideal. This is because the main concern at this stage was to manufacture functional instruments with the resources that were available. Manufacturing of miniaturised parts is more labour demanding and requires specialized manufacturing equipment, which would increase the cost of the prototype. Reducing the size of the sampler and designing more compact parts (solenoid pumps, cassette filter, electronic circuit, and stepper motor) can be considered in future designs. Some of the options are discussed in section 3.4.

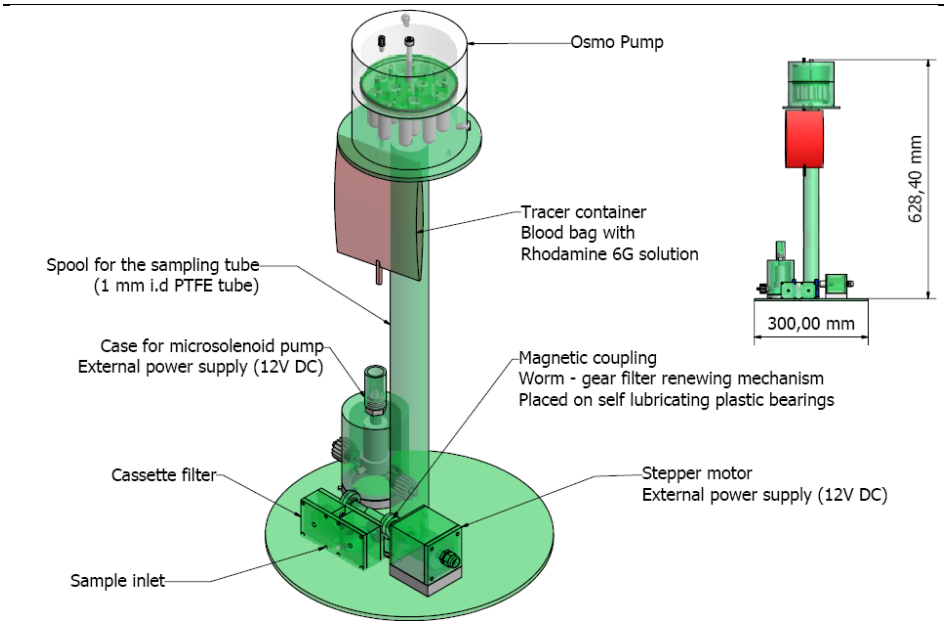


Figure 3-9: Prototype SCAWS (MK I).

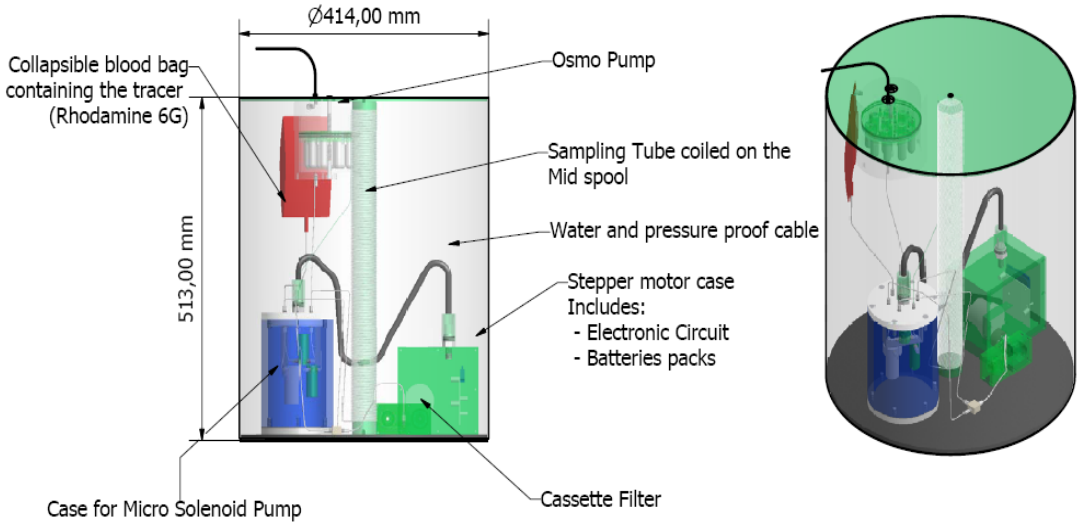


Figure 3-10: Complete prototype of the autonomous SCAWS (MK II).

Figure 3-11: MK II prototype of SCAWS. A: Parts of SCAWS; B: Configuration of Cassette filter and electronics case; C: Configuration of osmo pump and tracer injection system; D: Complete SCAWS prior deployment.

3.3 Lab tests of the SCAWS

The SCAWS features that were tested in the laboratory were:

- The pumping rate of the sampler.
- The extent of the dispersion and diffusion of soluble matter in the sampling tube.
- The performance of the cassette filter.

3.3.1 Pumping/Flow rate determination

The pumping rate of osmo samplers is a critical characteristic. The pumping rate determines the size of the daily sample and, consequently, the sampling resolution. Moreover, the pumping rate affects the dispersion of the sample in the tube. High flow rates in the sampling tube will increase the effect of smearing along the tube's walls and increase dispersion of samples. The overall flow rate of the osmo sampler depends on the number of osmotic pumps that are used in the sampler, and on the environment temperature (see chapter 2.2.4).

The SCAWS has twelve osmotic pumps, connected in parallel, which yield a theoretical flow rate of:

$$Q_{NOCS} = 12 \times Q_T \quad \textbf{3-4}$$

Where Q_T the theoretical delivery rate in μL/hr of each osmotic pump (eq. 2-8).

For the measurement of the flow rates the samplers were placed in temperature controlled water baths (precision ±0.02 ^{o}C).

The results from the temperature – flow rate experiments are presented in Table 3-1and Figure 3-12.

2005-2006 Measurements			2008 Measurements		
Temperature (^{o}C)	Flow rate (ml/d)		Temperature (^{o}C)	Flow rate (ml/d)	
6	0.8		5	0.9	
6	0.8		5	1	
6	0.8		5	1	Average : 0.98
6	0.8		5	1	Standard dev (σ): 0.05
6	0.8	Average : 0.80	10	1.3	
6	0.8	Standard dev (σ): 0.00	10	1.3	
10	0.9		10	1.3	
10	1		10	1.3	Average : 1.30
10	1	Average :0.98	10	1.3	Standard dev (σ): 0.00
10	1	Standard dev (σ): 0.05	15	1.5	
12	1.2		15	1.7	
12	1		15	1.6	
12	1.1	1.08	15	1.6	Average : 1.58
12	1	Standard dev (σ): 0.10	15	1.5	Standard dev (σ): 0.08
15	1.2		20	1.9	
15	1.3		20	1.9	
15	1.3	1.25	20	1.9	Average : 1.90
15	1.2	Standard dev (σ): 0.06	20	1.9	Standard dev (σ): 0.00
21	1.5		25	2.2	
21	1.6		25	2.3	Average : 2.27
21	1.7		25	2.3	Standard dev (σ): 0.06
21	1.7				
21	1.7	1.65			
21	1.7	Standard dev (σ): 0.08			

Table 3-1: SCAWS's flow rate - temperature relationship; experimental results

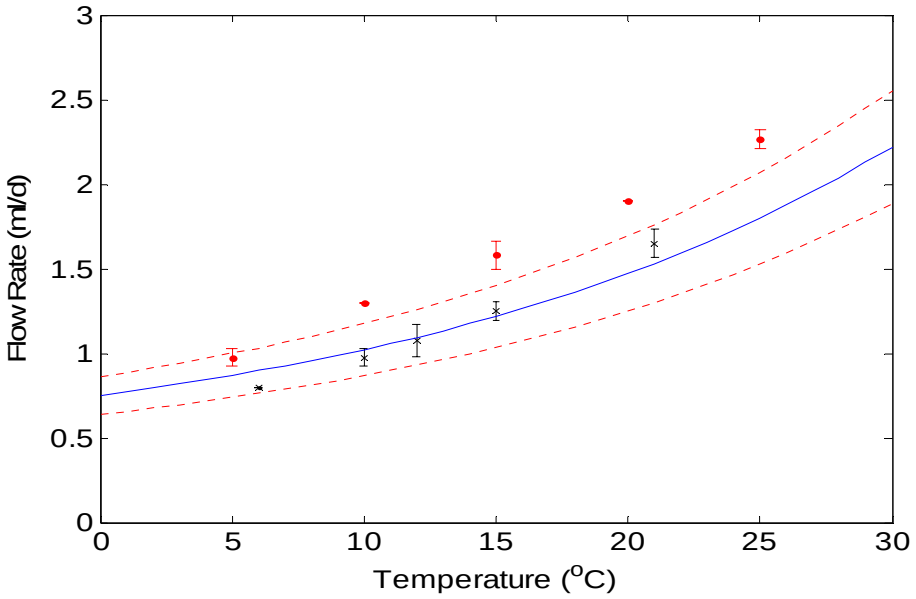


Figure 3-12: Flow rate evaluation of SCAWS. The solid line is the nominal/theoretical flow rate which is calculated from eq. 2.8. The dotted lines are the ±10% limits of the flow rate. Star points are measurements of the nominal flow rate in December 2005 with new osmotic pumps. The red dots are measurements of the flow rate in July 2008, with osmotic pumps that were used for more than one year. Error bars are 2σ (see Table 3-1).

From Figure 3-12 it can be seen that the first batch of osmotic pumps, yielded a flow rate within the ±10% of the theoretical flow rate. However different batches yielded a flow rate which was 20% higher than the nominal theoretical value and 5 – 10% above the maximum error. In both cases the pumping rate follows an exponential relationship with temperature. The results from the exponential fit are presented in Table 3-2.

The results indicate the necessity to evaluate the relationship between the pumping rate and temperature, whenever osmotic pumps are replaced. These results indicate that when the osmotic pumps are used for extensive periods (>1 year) their properties, which influence the flow rate of liquid across the membrane, alter, emphasizing the need for a time stamping device.

Model:	$y = a \cdot e^{(b \cdot x)}$ y is the Pumping rate and x is the Temperature	
Batch of osmotic pumps	December 2005	July 2008
Coefficient *a* (with 95% confidence bounds):	0.630	0.858
Coefficient *b* (with 95% confidence bounds):	0.046	0.0397
Correlation coefficient (R^2):	0.998	0.998

Table 3-2: SCAWS pumping rate exponential fit.

3.3.2 Diffusion and sample dispersion evaluation

The theoretical analysis of diffusion and dispersion of solutes was presented in section 2.3.2. The experiments from the first OsmoSamplers (Jannasch *et al.*, 2004) indicate that over a two month deployment concentration differences are integrated within a 1.5 day sample interval, and the Taylor dispersion model suggests that the "expansion" of the concentration profile after 1 week will be approximately 10 cm. It is necessary, however, to experimentally evaluate these phenomena for the SCAWS conditions.

To evaluate the diffusion and dispersion of the solutes two experiments in which the osmo sampler inlet was alternated between deionized water and solution with various concentrations of ions, were performed.

The first experiment lasted for five days. The inlet of the sampling tube was changed between deionized water and a 65 mM salt solution. Analysis of chloride in all the samples was conducted with Ion Chromatography – DIONEX® IC25 (see section 4.3). For this experiment the sampling tube was segmented according to the daily volume uptake record (see Table 3-3). The results are presented in Table 3-3 and illustrated in Figure 3-13.

	Volume/day (ml)	Length (cm)	Solution	Cl (mM)
sample 1	1.42	181	MQ H_2O	9.2
sample 2	1.39	177	NaCl sol.	68.1
sample 3	1.41	180	MQ H_2O	0.8
sample 4	1.43	182	NaCl sol.	65.2
sample 5	1.40	178	MQ H_2O	0.4

Table 3-3: Evaluation of the dispersion of chloride in the sampling tube during a five day period.

The results indicate that for a five days period, the diffusion and dispersion of Cl^- was minimal and the chloride aliquot remained within the expected tube length. The high concentration (9 mM) of the first sample is due to contamination of the deionized water container while switching the inlet tube from one container to the other. For this reason it was decided to use different tubes for each solution that were connected to the main sampling tube via a flexible connection. The increase, above Cl^- concentration in DI water that is observed in days 3 and 5 is related with the segmentation of the sampling tube and the effects of diffusion. The contribution of diffusion can be evaluated from the diffusion profile (Figure 3-13) that is produced from equation 2-11.

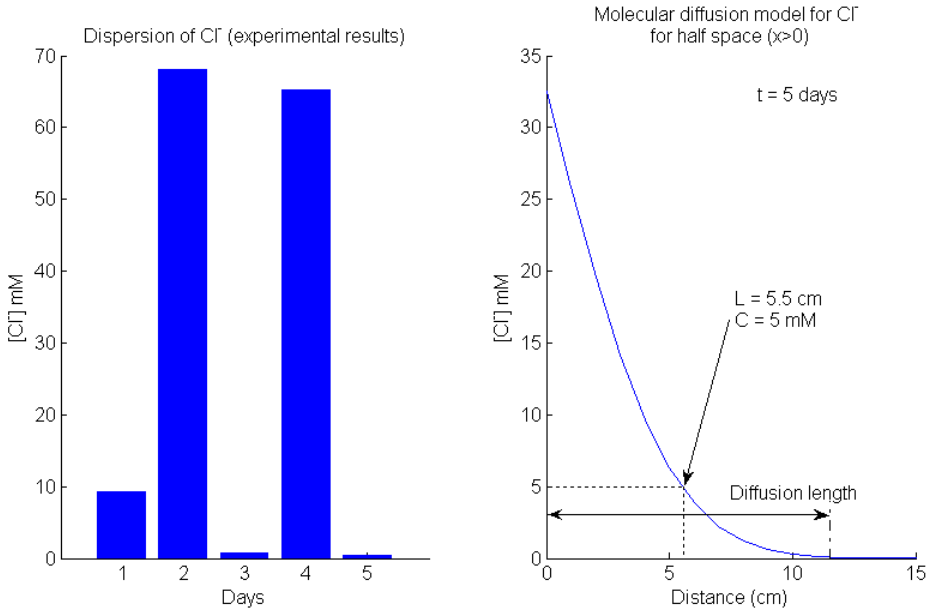


Figure 3-13: Results from the 5-day dispersion evaluation experiment. The molecular diffusion model is combined "Taylor" dispersion and molecular axial diffusion.

The second experiment but was for a longer period of time (18 days) and the test solution contained Br^-, NO_3^- and SO_4^{-2}. We used four test solutions, each of which contained the same concentration of all the analytes. The concentrations were 1 mg/l, 5 mg/l 10 mg/l and 15 mg/l. The sampling tube was segmented using the time stamping (rhodamine injection) concept. Results are presented in Table 3-4 and Figure 3-14.

	Measurements			Expected Value
	Br (mg/l)	NO_3^- (mg/l)	SO_4^{-2} (mg/l)	(mg/l)
Sample 1	0.0	3.1	1.0	1
Sample 2	0.0	0.0	0.7	0
Sample 3	14.1	16.2	14.4	15
Sample 4	5.9	3.7	6.0	5
Sample 5	0.6	0.1	1.3	0
Sample 6	0.3	0.0	1.1	0
Sample 7	0.0	0.0	0.6	0
Sample 8	4.3	5.2	5.9	5
Sample 9	0.0	0.1	0.1	0
Sample 10	0.0	0.0	2.4	1
Sample 11	0.9	0.7	1.1	0
Sample 12	10.7	10.4	11.1	10
Sample 13	0.0	0.0	0.4	0
Sample 14	0.0	0.1	0.0	0
Sample 15	0.6	0.3	1.4	1
Sample 16	0.0	0.0	0.5	0
Sample 17	0.0	0.0	0.1	0
Sample 18	0.0	0.0	0.0	0
Sum	***37.3***	***39.9***	***48.2***	***38***

Table 3-4: Concentrations of analytes of the dispersion - diffusion evaluation experiment. The expected value is the same for all analytes, as the solutions contain the same amount of each analyte. Zero (0.0) values are measurements below the detection limit. Relative errors for all analytes are presented in section 4.3.3.1.

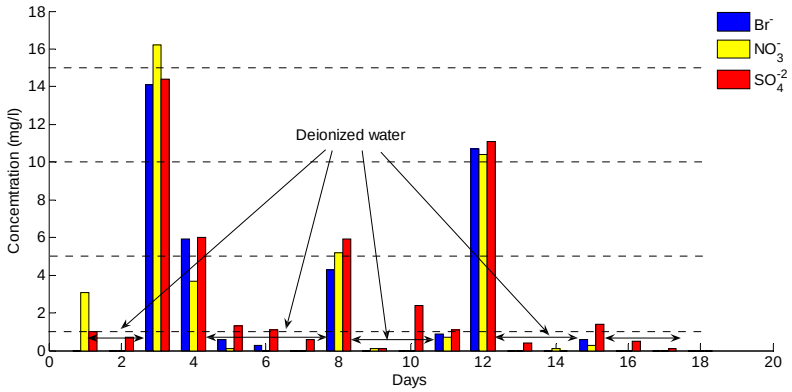


Figure 3-14: Evaluation of dispersion in the sampling tube. Dashed lines are the expected values (1, 5, 10, 15 mg/l).

The results from this experiment indicate the following:

- Overall temporal sampling resolution and the significant differences in concentrations of all three analytes are maintained during the period of the experiment.

- Small concentrations of analytes in the deionized water segments are due to diffusion and the fact that small differences in segmentation of the sampling tube will contaminate the deionized water segment.
- There is a carryover of SO_4^{-2}, which is most likely related to contamination, by the Rhodamine injection system (container, solenoid pump, specific rhodamine solution). This hypothesis is supported by the observation that the total measured concentration of SO_4^{-2} is 10 mg/l higher than the expected one. For this reason the rhodamine solutions that was used was analyzed on IC, and it was found that it contributes about 0.5 mg/l, with each injection.

3.3.3 Evaluation of the filtering device

The aim of the test on the filtering device was to evaluate the following issues:

- Degree of biofouling on the exposed nylon mesh
- Efficiency of the magnetic coupling
- Overall performance of the cassette filter

It is important to evaluate the degree and the rate of biofouling on the exposed filter because these will provide an estimate of how often the filter needs to be renewed. Three experiments were performed to evaluate the biofouling on the filter mesh. All three were conducted during spring (April – May), as during that period algae growth is favoured and biofouling reaches its peak.

In the first test, the entire cassette filter, equipped with the nylon mesh was placed in the sea (NOCS pontoon) for two weeks. This test gave an indication of the biofouling on the sampling orifice and the exposed nylon mesh. For the second test the nylon mesh was exposed directly to the seawater for periods ranging from one day up to four weeks. The third test aimed to identify whether the inner part of the nylon mesh that is rolled on the cassette filter and is not exposed directly to seawater, will be biofouled. For this test the nylon mesh strips were rolled on plastic drums and deployed at Southampton Docks for up to 8 weeks. Results from the three experiments are presented in Figure 3-15.

The sampling orifice remained clear, even after been submerged for two weeks in an environment which favours biofouling. The inner layer of the filter remained clear and unclogged after eight weeks of submersion. Given the fact that the filter will be renewed every 5 days, it can be assumed that the filtering device will not block, and sampling will be continuous. The results from the experiments suggest that biofouling of the nylon mesh (at least in a marine environments) will not affect sampling.

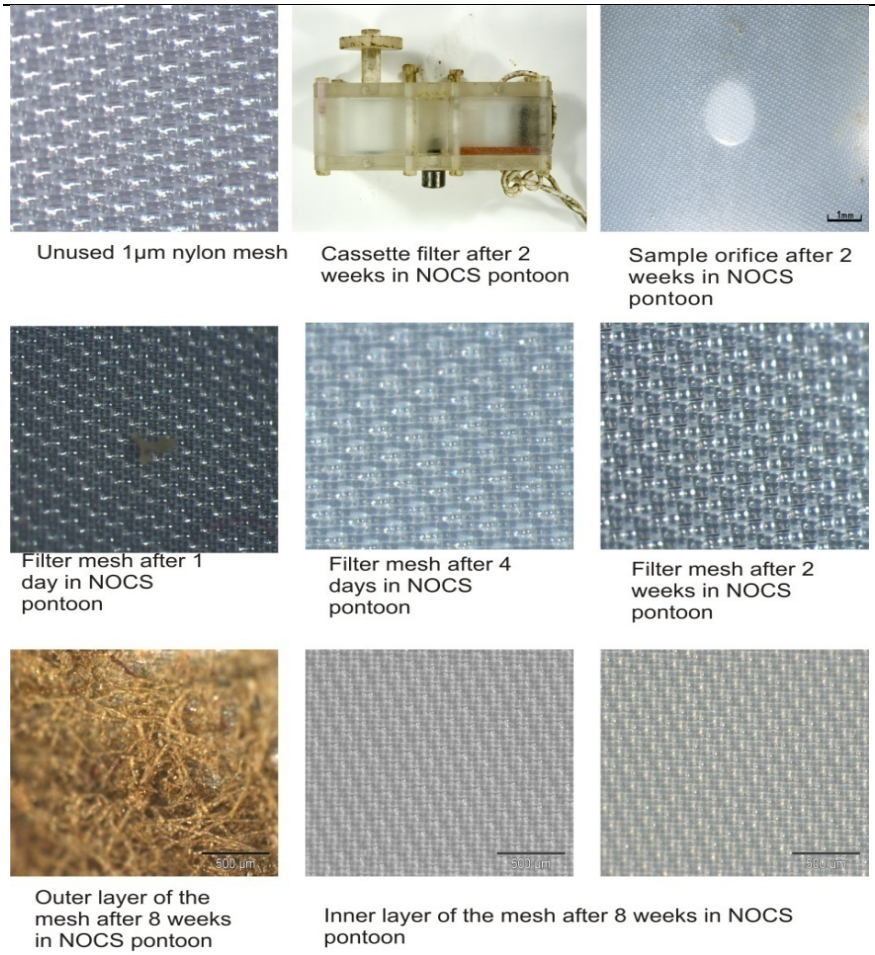


Figure 3-15: Evaluation of biofouling on the filtering medium.

In order to evaluate the efficiency of the filtering device, the cassette filter and the stepper motor were placed in a water tank, containing suspended sediment collected from a local river (Lymington River). The inlet of the filter was connected to a peristaltic pump, which operated continuously, so that water flow through the filter was continuous. The flow rate of the pump was approx. 0.5ml/s, which is higher than the osmo samplers flow rate (1ml/d). Hence the test conditions are the worst case scenario, as the amount of water that passes through the filter is much higher than the real conditions.

Evaluation was based on measurement of suspended solids of the ambient water and the filtrate. The filter was renewed initially after three days, then after five days and finally after 10 days. Filtrate samples were collected prior to renewal of the filtering medium and after the renewal, so as to evaluate whether it is necessary to renew the filter more frequently. The experiment lasted for three weeks. The results are presented in Figure 3-16. The ambient suspended sediment concentration is approximately 4 mg/l, and the concentrations of the filtrates in all samples were lower. The filtrates that exhibit higher suspended solids concentrations are the ones that were

collected when the nylon mesh has not been renewed and used for more than one week. This observation indicates that suspended matter gradually passes through the mesh; hence it is necessary to renew the filter every five days.

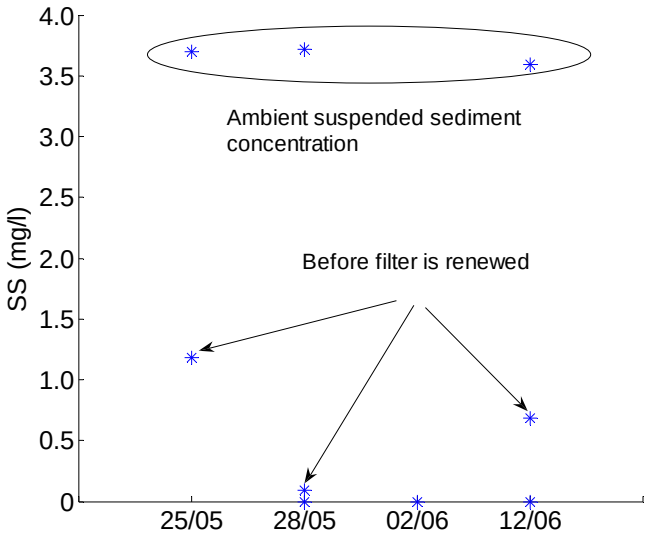


Figure 3-16: Evaluation of the filtering efficiency.

3.3.4 Alternative tests and solutions

During the design and development of the SCAWS, various solutions were considered, in order to efficiently tackle the associated challenges. Those presented in the previous sections were found to be the most efficient. In the following paragraphs, there is a presentation and short discussion of the alternative options that were tested, but ultimately rejected for the SCAWS.

3.3.4.1 Alternative tracing – time stamping media

The experiments with alternative materials as time stamps/tracers follow the same basic idea that was presented in section 3.3.2. Besides rhodamine 6G and fluorescein, the following materials were tested:

- **Fluorescent microspheres:** These are used in various applications (e.g. microbiology, flow cytometry) to stain biological matter, which can then be detected under a fluorescent microscope. For the SCAWS the idea is similar. Microspheres (3 μm diameter) were mixed with deionized water (50 μl of the microsphere stock solution in 50 ml DI water) and injected with the micro – solenoid pump in the sampling tube. The microspheres should flow along the sampling tube and follow the exact flow rate of the water sample during the

deployment period. As the Teflon sampling tube is transparent, it will be possible to detect the fluorescence microspheres under a fluorescence microscope and segment the sampling tube where the spheres are detected. The initial test was to identify whether the microspheres in the sampling tube could be detected with the fluorescent microscope. This proved possible, so it was decided to test them in real osmo sampling conditions. The test lasted for two weeks, but final results were not encouraging. The main problem is that the microspheres attach to the tube walls, so it was not easy to identify the main part that was originally injected. Another difficulty was that the detection of the microspheres under the fluorescence microscope was not very practical. The sampling tube had to pass under the microscope, but it was very difficult to place the sampling tube under the microscope and at the same time detect the microspheres. The data from this experiment were not recorded visually because the fluorescent microscope we used was not equipped with a photographic camera.

- **Silicone Oil:** Tracer addition provides the means to time stamp the samples, but it does not separate the samples. Separating the samples during the deployment period would be a major improvement for osmo sampler technology, as this would prevent diffusion of any kind between samples and dispel any ambiguities concerning sample identification and sampling tube segmentation. One option would be to inject a hydrophobic substance that is able to act as physical barrier between the samples. The main concern with this application is that part of the oil might stick to the Teflon tube walls. This was confirmed with an experiment, were silicone oil was injected in the sampling tube, with the micro solenoid pump. The initial volume of silicone oil (50 μl) occupied 5.5 cm of the sampling tube. After 1 day the length has been reduced to 5.4 cm and after a week the strip's length was 3.5 cm, indicating that oil became attached to the sampling tube walls.

  More important though is the fact that most of these oils will contaminate the samples because they are not chemically clean. Besides that, it will be necessary to separate the oil from the water before analyzing the samples. This might reduce the sample volume, which is not desired as the volume is already small.

3.3.4.2 First cassette filter drive mechanism

The first mechanism that was driving the cassette filter was based on a worm gear configuration as is seen in Figure 3-17.

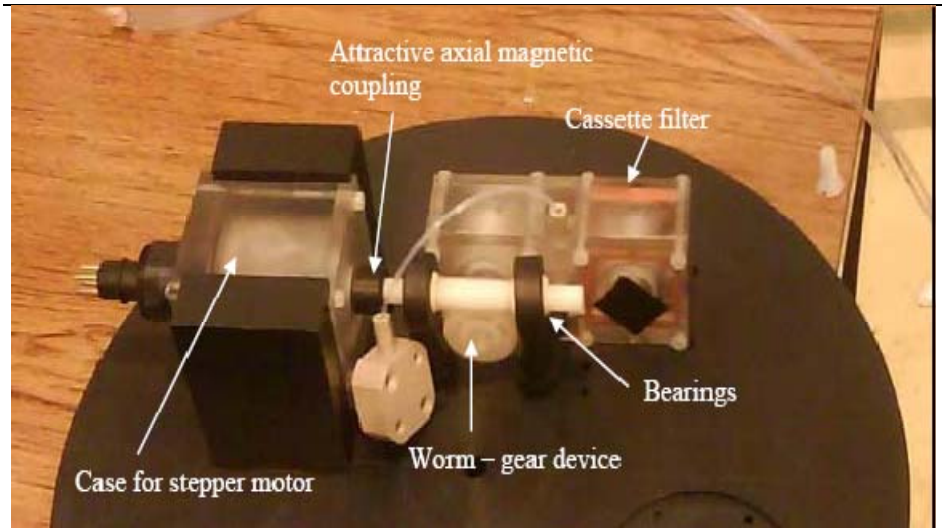


Figure 3-17: Configuration of the first filtering renewal mechanism.

The stepper motor's characteristics are

Model:	Nanotec SP1518M0204
Type:	Bipolar
Rated Voltage (V DC):	12
Step angle (^{0}):	18
Holding torque (g cm):	35
Current per phase (mA):	240

The motor was chosen because it is small and has low power consumption. The worm and gear were from Delrin. The reduction ratio is 1:16 ratio, which can increase the output torque 10 fold (from 0.0034 Nm to 0.037 Nm (see APPENDIX for calculations)). The necessary torque to drive the cassette filter is less than 0.01 Nm, so the system is adequate. The first lab tests and the first deployments were positive and confirmed the theoretical calculations. However, the main problem with the above design is that the worm gear configuration is exposed to the environment. This has the following drawbacks:

- Biofouling can block the worm/gear configuration,
- Movement of the sampler, due to water motion, misaligns the configuration of the worm gear mechanism, which can restrict the movement and create friction that the stepper motor cannot overcome.

It was decided therefore to use a geared stepper motor which consumes more power but is much more robust and powerful (Holding torque = 0.135 Nm).

3.4 Need for improvements and optimization

What was presented in the previous sections of this chapter is a SCAWS prototype. This instrument has been used to identify whether osmo samplers are reliable and to identify whether the innovative features that we have added are performing within expectations. Lab tests and deployments in real aquatic environments (see next sections) prove that the SCAWS can be a reliable and useful sampling device. However, there are some features that need to be improved. The features that might be improved, to enhance the sampler performance are presented below.

- *Gas injection as a time stamp:* During lab tests and field deployments, air can be trapped in the sampling tube, mainly due to switching of the sampler's inlet from one solution to the other. Air is not desired to be trapped in the sampling tube, because in deployments at deep environments, the air/gas will decompress during recovery causing rapid movement in the sample tube, causing dispersion and distortion of the samples and the sampling sequence. We did not experience such problems during lab tests and deployments, because all of them were in shallow – surface waters. What was interesting was that when the air bubble was added before or after the rhodamine strip, dispersion of the colour along the sampling tube was prevented, which is similar to how air/gas bubbles are used to separate samples in Nutrient Autoanalyzers. Therefore, if gas or air is injected in the sampling tube at a predetermined frequency the gas bubbles could trap the sample, separate the samples and at the same time preserve them. Such a time stamping/segmentation system is ideal for shallow water deployments (<5m) were pressure differences will not cause problems during recovery. The main challenge for this application is to design an effective gas injection device that will meet the characteristics of the osmo sampler and to find a gas which is chemically inert and clean, so that it does not contaminate the samples. Also because Teflon is permeable to gases it will be preferable the use a heavy gas with a low diffusion coefficient through Teflon (e.g argon, xenon). Design and development of the gas injection system will be considered in future versions of the SCAWS.
- *Acid – Preservative addition:* The importance of acid addition to preserve "osmo" samples has been demonstrated by Jannasch et al. (2004). An acid addition device should be included in the osmo sampler if the samples are to be analysed for redox sensitive elements (e.g. iron, manganese). The same device using a different preservative (e.g. formaldehyde, formalin) could be used if the sampler is focusing on biogeochemical or microbiological sampling. However acidic solutions could leach elements from any fine particles (<1 μm) that might pass through the filter. Hence, the decision regarding whether or not to add acid is not clear, and will depend on the objectives of the sampling.
- *Minimize the Sampler:* The SCAWS prototype is a relatively big instrument. Reducing the size of the sampler will make it more versatile, easier to handle and prepare. Apart from the osmo pump, all the other parts can be minimized. The cassette filter can be smaller, which

will reduce the power requirement to renew the filter mesh. Consequently the stepper motor and the stepper motor case can be reduced. The new version of the data logger, is already smaller than the one we used in our prototype. Minimizing the dimensions of the sampler, and developing a compact sampler will be a priority for the new version.

4 Evaluation Tools – Analytical Methods

4.1 Rationale

The following criteria were considered for the selection and development of the analytical methods:

- *The methods will provide the necessary means to evaluate the SCAWS's performance.* It is not within the scope of the project to develop entirely new protocols, but to modify existing ones so that they can be used for the collected samples.
- *Small sample volumes.* This is an important limitation for osmo samplers, as stated in previous chapters
- *Matrix and background interferences.* Saline matrices can interfere with some analytes, e.g. isotopic interferences and deposition of salts on skimmer cones, due to high salt concentrations, in Inductively Couple Plasma Mass Spectrometry (ICP-MS) can reduce sensitivity and increase detection limits.

In addition, issues such as availability of the analytical instruments, the cost of the analysis, and the analysis time, were also considered.

Based on the above, it was decided to use Ion Chromatography, to determine major anions and cations, and Inductively Couple Plasma Mass Spectrometry (equipped with a collision/reaction cell), for major cations (Na, K, Mg, Ca) and a suit of trace metals.

4.2 Auxiliary equipment, analytical accessories

Auxiliary equipment and miscellaneous accessories include:

- High density polyethylene bottles (Nalgene®) in various sizes. These were used for manual sampling and storage of the samples, preparation and storage of standard solutions for the analytical methods. Bottles that were used for samples for ICP-MS analysis were soaked at least for 24 hours with 10% HNO_3 (Aristar grade), rinsed thoroughly with deionized water and dried. Bottles for IC samples were rinsed only with deionized water and dried. All bottles were kept in air tight plastic bags.
- Cellulose acetate or cellulose nitrate 0.45 μm filters, 40 mm diameter. There was a concern whether cellulose nitrate filters would contribute to nitrate measurements. Analysis of deionized water that passed through the filters did not indicate any contamination (nitrate concentration in these samples was below the lower level of detection (10 μg/l) for the IC systems we used).

- Portable filtering equipment for in situ filtration of manually collected water samples. Equipment includes a manually operated vacuum pump, a filter holder for 40 mm diameter circular filters, and flask for the filtered water. All the wetted parts were made from Teflon, so they could be acid washed and thus be made suitable for trace metal – clean chemistry.
- All HNO_3 solutions were made from Aristar (or better) quality 69% HNO_3 and stored in acid cleaned nalgene bottles.

4.3 Ion Chromatography

4.3.1 System characteristics

Ion Chromatography (Small *et al.*, 1975; Gjerde *et al.*, 1979) was used for the determination of major anions (F^-, Cl^-, Br^-, NO_3^-, PO_4^{-3}, SO_4^{-2}) and cations (Na^+, K^+, Mg^{+2}, Ca^{+2}). Two DIONEX® Ion Chromatography systems were used; one is a single column system for anions analysis, which is operating in University of Southampton's School of Ocean and Earth Science (DIONEX® IC25), and the other one is a dual system able to determine both anions and cations, which is operating in the University of Bristol, School of Geographical Sciences (DIONEX® DX500). The technical characteristics of the systems are presented in Table 4-1 and Table 4-2.

System	*DIONEX IC25*	*DIONEX DX500*
Pump	Isocratic IS25 DIONEX pump (0 - 5000 psi)	Gradient pump GP50 (0 - 5000 psi)
Flow rate	1 ml/min	1.25 ml/min
Operating pressure	1800 psi	1980 psi
Sample loop	250 μl	100 μl
Sample injection	Manual, Autosampler AS40	Autosampler AS40
Injection valve	Rheodyne 6 way valve	Rheodyne 6 way valve, which switches with compressed nitrogen
Columns	Guard column: AG14 4x50 mm Analytical column: AS14 4x250 mm	Guard column: AG-11-HC 4x50 mm Analytical column: AS-11-HC 4x250 mm
Eluent	8 mM $NaHCO_3$/ Na_2CO_3	30 mM NaOH
Suppressor	ASRS ultra II 4-mm Self regenerating (Electrolysis of MQ water by applying 100 mA DC current)	ASRS ultra II 4 – mm Self regenerating (Electrolysis of MQ water by applying 100 mA DC current)
Analysis time	20 min	15 min
Detector	CD 20 Conductivity cell (0 – 1000 μS/cm)	CD 20 Conductivity cell (0 – 1000 μS/cm)
Software	Chromeleon 6.2 Integrator and Data management system	Chromeleon Integrator and Data management system

Table 4-1: Characteristics of IC systems for anions

System	*DIONEX DX500*
Pump	Gradient GP50 (0-5000 psi)
Flow rate	1 ml/min
Operating pressure	1064 psi
Sample loop	100 µl
Sample injection	Autosampler AS40
Injection valve	Rheodyne 6 way valve, which switches with compressed nitrogen
Columns	Guard column: CG12A 4x50 mm Analytical column: CS12A 4x250 mm
Eluent	20 mM Methanesulfonic Acid
Suppressor	CSRS ultra II 4 mm Self regenerating (Electrolysis of MQ water by applying 50 mA DC current)
Analysis time	15 min
Detector	Conductivity cell (0-2000 µS/cm)
Software	Chromeleon Integrator and Data management system

Table 4-2: Characteristics of IC system for cations

In both systems eluents were stored in pressurized containers (5 – 8 psi head pressure), so that eluent flow is smoother and background noise is limited. The IC25 system uses filtered air to pressurize the eluent and the DX500 systems uses high purity compressed helium at 5-8 psi. Helium retains an inert atmosphere and degasses the eluent, so that signal noise is further reduced. Both systems' pumps were primed prior to analysis, so that any air bubbles trapped in the system are removed before analysis. After priming, the systems were left for 15 minutes to reach equilibrium between eluents and ion exchange beds (columns and suppressor).

Calibration standards were prepared either from a mixed standard stock solution (DIONEX® Combined seven anion standard II or Combined for cation standard), or from stock solution of individual elements (Fisher Scientific). The concentration of analytes in the stock DIONEX® combined standards were:

Combined Seven Anions (IC25)		Cations (DX500)		Combined Three Anions (DX500)	
Analyte	mg/l	Analyte	mg/l	Analyte	mg/l
F^-	20	Na^+	200	Cl^-	30
Cl^-	100	K^+	25	SO_4^{-2}	150
NO_2^-	100	Mg^{+2}	500	NO_3^-	100
Br^-	100	Ca^{+2}	500		
NO_3^-	100				
PO_4^{-3}	200.0				
SO_4^{-2}	100				

4.3.2 Sample preparation

Manual samples were filtered through 0.45 μm cellulose nitrate filters. Because sample volume might be lost with filtration (dead volumes in filtration apparatus, mishandling), osmo samples were not filtered in the lab. SCAWS samples were not filtered in the lab. However, the sample vials for the DIONEX AS40 Autosampler are equipped with 0.45 μm filter end caps, so all samples analyzed with the AS40 Autosampler were filtered through this size filters.

4.3.2.1 River water samples

River water samples that were collected manually did not require dilution, as most analytes were within the analytical columns maximum concentration limit. Samples from the osmo sampler were diluted 10 fold, in order to increase the volume of the sample, and at the same time retain the analytes concentrations at levels above the methods detection limit.

4.3.2.2 Sea water samples

Ion chromatography is not a standard technique for analysis of major ions in sea water. The main reason is the very high concentrations of sodium and chloride, which are 2.5 orders of magnitude above the highest concentration that our analytical columns can handle ($[Cl^-]$ in seawater is approx 0.5 M, maximum concentration for column is approx. 2 mM). In addition, the high concentration of chloride increases and spreads the chloride peak, to a point where it interferes with ions that elute close to chloride, e.g bromide and nitrate. Therefore, samples need to be diluted at least 250 fold and usually 500 fold so that the columns do not overload. With such high dilutions the nitrate concentrations of diluted samples fall close to, or even below, the method's detection limit, and the phosphate concentrations are not detectable. Therefore the NO_3^- results from sea water samples obtained with ion chromatography are considered to be indicative rather than completely reliable.

Determination of nutrients with standard analytical techniques (Morris and Riley, 1963) was possible only for manual samples, because osmo samples were coloured with rhodamine (see section 3.2.3), which interferes with the colour that is produced when the reagents are added for the analysis.

4.3.3 Method evaluation and performance

The method evaluation includes the estimation of errors, the detection limits, calibration data and comparison between the two IC systems (DX500 and IC25).

4.3.3.1 Precision and Accuracy

The bias, precision and accuracy of an analytical method can be determined with analyses of replicate reference materials and standards. Standard deviation and relative standard deviation (RSD) (equations 4-1 and 4-2) of these measurements provide an initial indication of the systems performance.

Standard Deviation (σ)

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{(N-1)}} \qquad \textbf{4-1}$$

Relative Standard Deviation (RSD)

$$\text{RSD} = \frac{\sigma \times 100}{\bar{x}} \qquad \textbf{4-2}$$

Where N is number of samples, x_i is value of a sample, N is the number of samples, $\bar{x}$ is the arithmetic mean of the samples.

Results from measurements of a seven anion mixed standard, on the DIONEX® IC25 are presented in Table 4-3.

The RSD's in Table 4-3 can be used to calculate the errors for the IC25 system.

	Measurements (mg/l)						
	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{-3}	SO_4^{-2}
DIONEX® Combined Seven Anion Mixed standard II Dilution 1:400	0.053	0.26	0.26	0.26	0.27	0.52	0.26
	0.051	0.25	0.25	0.26	0.25	0.52	0.26
	0.051	0.26	0.26	0.26	0.26	0.51	0.26
	0.051	0.25	0.26	0.26	0.27	0.52	0.26
	0.053	0.25	0.26	0.26	0.25	0.51	0.26
	0.050	0.25	0.26	0.26	0.25	0.52	0.26
	0.053	0.26	0.26	0.26	0.26	0.52	0.26
	0.051	0.28	0.26	0.26	0.26	0.52	0.27
	0.052	0.26	0.27	0.26	0.26	0.53	0.26
	0.052	0.25	0.25	0.26	0.25	0.52	0.26
Mean (mg/)l	0.052	0.26	0.26	0.26	0.26	0.52	0.26
Standard Deviation (σ) (mg/l)	0.001	0.009	0.004	0.002	0.007	0.005	0.004
RSD (%)	***1.8***	***3.4***	***1.7***	***0.8***	***2.9***	***1.0***	***1.6***

Table 4-3: Measurement of Relative Standard Deviations for DIONEX IC25 system.

For the DX500 system, results from similar measurements are presented in Table 4-4 and Table 4-5

DIONEX® Combined Three Anion Mixed standard Dilution 1:100	Measurements (mg/l)		
	Cl^-	SO_4^{-2}	NO_3^-
	0.26	1.43	1.20
	0.25	1.44	1.12
	0.24	1.44	1.12
Mean (mg/)l	0.25	1.44	1.14
Standard Deviation (σ) (mg/l)	0.01	0.01	0.04
RSD (%)	3%	1%	3%

Table 4-4: Precision and accuracy for anions of the DX500 system.

DIONEX® Combined Four Cation Mixed standard Dilution 1:100 for Na^+ And 1:5000 for K^+, Mg^{+2}, Ca^{+2}	Measurements (mg/l)			
	Na^+	K^+	Mg^{+2}	Ca^{+2}
	2.16	0.08	0.06	0.13
	2.03	0.08	0.06	0.18
	2.03	0.08	0.06	0.12
Mean (mg/)l	2.06	0.08	0.06	0.13
Standard Deviation (σ) (mg/l)	0.05	0.00	0.00	0.01
RSD (%)	3%	1%	2%	5%

Table 4-5: Precision and accuracy for major cations of the DX500 system.

4.3.3.2 Detection Limits

According to the Standard Methods for the Examination of Water and Wastewater (Eaton *et al.*, 2005), there are several detection levels that can be used to demonstrate the quality characteristics of an analytical method. These are:

- Instrument Detection Level (IDL): Analyte concentration that produces a signal three times greater than the standard deviation of the mean noise levels
- Lower Level of Detection (LLD): Analyte concentration that produces a signal sufficiently large that 99% of the trials will be detectable.
- Limit of Quantification (LOQ): The concentration level above which quantitative results may be obtained with a specific degree of confidence.

The ion chromatography system that was used, determination of the LLD was based on analysis of the low concentration standard, and identifying at which concentration peaks were not reproducible and detectable. Results indicated that the lowest detectable concentration for all analytes is 10 μg/l. For this reason it was decided to measure how the IC25 system performs at 5×LLD (50 μg/l). Results are presented in Table 4-6.

DIONEX® Combined Seven Anion Mixed standard II Dilution 1:2000	Measurements (µg/l)						
	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{-3}	SO_4^{-2}
	9	48	59	46	53	90	54
	7	52	43	42	50	86	59
	12	50	44	46	45	91	53
	12	48	42	44	46	84	48
Mean (µg/l)	10	49	47	45	48	88	54
Standard Deviation (σ) (µg/l)	0.2	2	8	2	4	3	5
RSD (%)	25	4	17	4	7	4	9

Table 4-6: Detection Limit for IC25 system.

For the DX500 system measurements of low concentration standards are presented in Table 4-7.

	Na^+	K^+	Mg^{+2}	Ca^{+2}	Cl^-	SO_4^{-2}	NO_3^-
Standard 1	31.5	46.5	13.7	26.4	17.6	*33.6*	35.9
Na = 23.0 µg/l, K = 39.0 µg/l,	29.1	41.6	12.4	21.2	18.2	29.2	33.9
Mg = 12.0 µg/l, Ca = 20.0 µg/l,	*35.7*	44.9	11.9	24.8	*12.1*	*35.4*	34.5
Cl= 17.5 µg/l, SO_4 = 24.0 µg/l	27.8	42.6	12.4	28.0	*63.0*	26.9	*129.4*
NO_3 = 31.0 µg/l	27.6	43.9	12.9	28.4	*52.5*	28.5	38.9
	29.7	42.8	13.5	27.4	15.3	27.2	33.4
Mean (µg/l)	30.2	43.7	12.8	26.0	17.1	27.9	35.3
Standard Deviation (σ) (µg/l)	3.0	1.8	0.7	2.7	1.5	1.1	2.2
RSD (%)	10%	4%	5%	10%	9%	4%	6%
	Na^+	K^+	Mg^{+2}	Ca^{+2}	Cl^-	SO_4^{-2}	NO_3^-
Standard 2	45.4	78.8	28.2	39.7	36.1	56.8	60.4
Na = 46.0 µg/l, K =78.0 µg/l,	43.4	77.8	25.9	46.8	*11.2*	*39.0*	*28.3*
Mg = 24.0 µg/l, Ca =40.0 µg/l,	42.4	78.7	27.7	38.0	29.9	54.1	59.2
Cl= 35.5 µg/l, SO_4 = 48.0 µg/l	44.5	70.7	24.9	43.6	34.0	56.6	60.8
NO_3 = 62.0 µg/l	46.2	83.7	27.5	41.1	40.6	58.3	66.4
	48.9	75.8	27.7	55.5	*48.2*	61.4	68.2
Mean (µg/l)	45.1	77.6	27.0	44.1	35.1	57.5	63.0
Standard Deviation (σ) (µg/l)	2.3	4.3	1.3	6.4	4.5	2.7	4.0
RSD (%)	5%	5%	5%	14%	13%	5%	6%

Table 4-7: Detection limit for the DX500 system. Values in red – italics were considered outliers (>2σ from the mean) and were not included in calculations.

From the above results it is evident that both systems are reliable, when concentrations are about 2 or 3 times the LLD. It should be noted that concentration of analytes in the real samples, were considerably higher than 3xLLD.

4.3.3.3 Calibrations

Linear equations (y = a·x or y = a·x + b) were used to calibrate the IC response for all the analytes. Linearity was not affected by large concentration differences between the low concentration standard and the high concentration standard, but correlation coefficients were better when the calibration range did not exceed 2 orders of magnitude (e.g. low standard 0.1 mg/l, high standard 2 mg/l).

Results from some of the calibrations are presented in Table 4-8 and Table 4-9.

Analyte	Cal.Type	Points	Concentration of Standards (mg/l)	Cor. Coef. (%)	Slope
F^-	Linear	4	5 – 10 – 20 – 50	99.98	2.58
Cl^-	Linear	4	5 – 10 – 20 – 50	99.99	2.23
NO_2^-	Linear	4	5 – 10 – 20 – 50	99.92	1.01
Br^-	Linear	4	5 – 10 – 20 – 50	99.95	0.90
NO_3^-	Linear	4	5 – 10 – 20 – 50	99.95	1.19
PO_4^{-3}	Linear	4	5 – 10 – 20 – 50	99.95	0.63
SO_4^{-2}	Linear	4	5 – 10 – 20 – 50	99.95	1.49

Table 4-8: Calibration results from 3rd Osmo Deployment (IC25 System)

Analyte	Cal.Type	Points	Concentration of Standards (mg/l)	Cor. Coef. (%)	Slope
Na^+	Linear	5	5 – 10 – 15 – 20 – 25	99.98	0.91
K^+	Linear	4	0.1- 0.5 – 1.0 - 2.0	99.99	0.54
Mg^{+2}	Linear	5	0.2 – 0.5 – 1 – 2 – 5	99.99	1.43
Ca^{+2}	Linear	5	0.1 – 0.25 – 0.5 – 1 – 2	99.99	0.94

Table 4-9: Calibration results from 3rd Osmo Deployment (DX500 system).

4.3.3.4 Comparison of the two IC systems

Comparison of results between the two DIONEX IC systems provides the means of evaluating how reliable the results are. As presented in Table 4-1, the two systems have different operating conditions, so if differences between the results are small, results from both systems can be considered to be reliable. Statistical tests such as paired t-tests can be used to compare methods (Miller and Miller, 1988), but these methods compare means of normal distributions. Linear regression or 1:1 comparison is preferred. Results from this comparison for Cl^-, SO_4^{-2}, and NO_3^- results obtained from the two IC systems are presented in Figure 4-1 and Table 4-10.

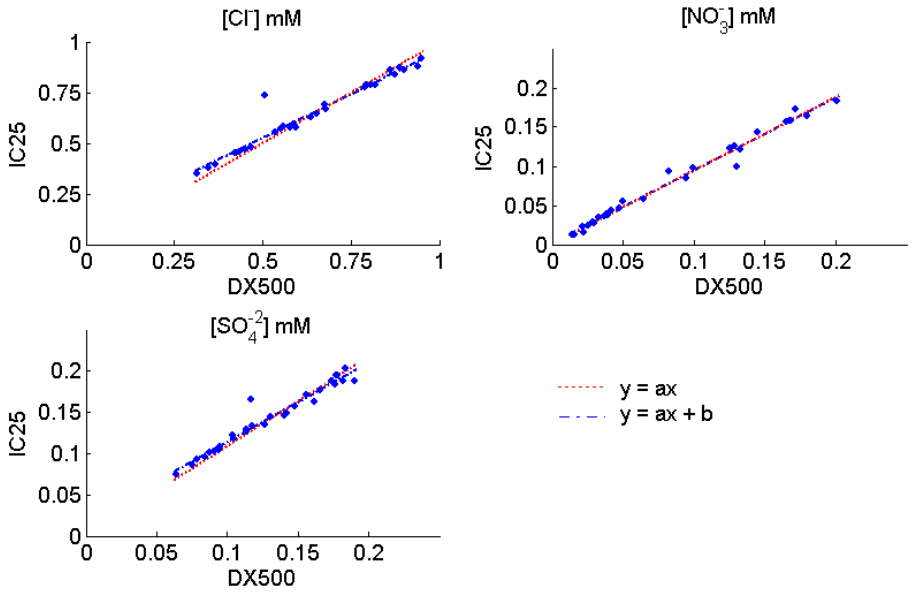


Figure 4-1: Comparison between the two IC systems. These results are from the one month river water deployment, and illustrate the good agreement between the two IC systems. Regressions were performed using the least squares method.

Parameters (95% confidence level)		DX500 vs IC25		
		Cl^-	SO_4^{-2}	NO_3^-
y = ax	slope (a)	0.9987	1.0884	0.9987
	R^2	0.9152	0.9326	0.9152
y=ax+b	slope (a)	0.8595	0.96	0.8595
	intercept (b)	0.0963	0.0181	0.0963
	R^2	0.9422	0.9511	0.9422

Table 4-10: Linear regression results from IC systems comparison.

The above analysis was based on the principles that Miller (Miller and Miller, 1988) suggests for such comparisons. The main requirement is that the most precise method is plotted on the x axis (independent variable). As relative errors in both systems are similar, the two data sets were plotted against each other in both ways. The ideal situation is when b = 0 and a = R^2 = 1.

The results indicate that for both correlation options, there is a good agreement between the two systems. Correlation coefficients are > 0.90 indicating good agreement of the two systems and the methods. Slopes are approaching 1, indicating that calibrations of the methods do not entail systematic errors. Intercepts on the y = ax+b model are low, which indicates that systematic analytical errors are low. This further strengthens the hypothesis that the two methods agree and results from both systems are reliable.

4.4 Collision – Reaction Cell ICP-MS (cr ICP-MS)

Over the past twenty years Inductively Couple Plasma Mass Spectrometry (ICP-MS) has become one of the most powerful analytical techniques for elemental and isotopic analysis of a variety of sample types (water samples, leachates, samples from digestions etc.). A major advantage of the method is that it provides simultaneous analysis of many elements using a small amount of sample. Detection limits for most analytes can be low (nM or pM), and performance of the instrument for certain analytes, comparing to other analytical methods, is enhanced (errors are lower).

Analysis of certain analytes (e.g. trace metals) in fresh water samples with ICP-MS has become a standard method (method 3125 (Eaton *et al.*, 2005), U.S EPA methods 200.8 and 6020).

However there are restrictions on the use of ICP-MS, which are mainly due to polyatomic interferences. These interferences might be related either to the matrix of the sample (e.g seawater, high organic content) or to the fact that the isotope of interest is very similar to some of the substances that are created from the ionization process (Horlick and Montaser, 1998). Examples of such interferences are presented in Table 4-11.

Analyte Isotope	Principle Interference	Relative abundance (%)
^{24}Mg (	$^{12}C^{12}C$	78.99
^{27}Al	$^{12}C^{14}N^{1}H$	100
^{39}K	$^{38}Ar^{1}H$	93.26
^{40}Ca	^{40}Ar	96.94
^{51}V	$^{35}Cl^{16}O$	99.75
^{52}Cr	$^{40}Ar^{12}C$, $^{36}Ar^{16}O$	83.79
^{55}Mn	$^{40}Ar^{14}N^{1}H$, $^{38}Ar^{17}O$	100
^{56}Fe	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$	91.72
^{63}Cu	$^{40}Ar^{23}Na$	69.17
^{75}As	$^{40}Ar^{35}Cl$	100

Table 4-11: Polyatomic interferences for some analytes when analyzed on ICP-MS (www.thermo.com)

The standard technique to overcome this problem is to measure the signal of the analyte at an interference free isotope (e.g measure ^{54}Fe or ^{57}Fe instead of ^{56}Fe) and subtract the fraction that corresponds to the interference from the signal of the quantifying isotope. Generally this technique produces good results, but when concentrations of analytes are at the μg/l level and matrices are complex the method becomes unreliable and sensitivity is compromised.

During the last 5 years, the collision –reaction cell method has been developed, which can reduce the polyatomic/isobaric interferences in ICP-MS systems. With this method a second gas (e.g. Helium or Hydrogen) is introduced in the ionization cell. The second gas can reduce interferences either by collisional dissociation (He) or by simple reaction between argon based molecular ions and hydrogen.

The crICP-MS is becoming a popular analytical technique, which expands the capabilities of ICP-MS instruments, so that analysis of new analytes (e.g. Ca, Fe) and samples with more complex matrices (e.g seawater samples, digests), is more reliable (Garbarino and Cree, 2006).

Concerning our project, a crICP-MS system was used for the determination of the following analytes:

- Major Cations: ^{23}Na, ^{24}Mg, ^{39}K, ^{40}Ca,^{43}Ca, ^{44}Ca
- Trace Metals: ^{55}Mn, ^{56}Fe, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{238}U

Major cations are important indices for environmental and geochemical processes in fresh waters, so their determination was necessary. Trace metals are equally important in geochemical and environmental processes, because of their high reactivity with other substances in water (hydroxo complexes, ligands biovailability (Drever, 1988; Stumm and Morgan, 1996)).

4.4.1 System Characteristics

The ICP-MS system was the Agilent 7500 ce ICP-MS system (University of Portsmouth, School of Earth and Environmental Sciences), which is equipped with an Octopole Reaction System (ORS) to reduce polyatomic/isobaric interferences. The instruments technical details and operating conditions are presented in Table 4-12.

Standards were prepared from individual stock solutions, specified for ICP-MS analysis (matrix is 2% Aristar HNO_3). The reference material that is used for the evaluation of the system and the method is a certified Riverine water Reference Material for Trace Metals (SLRS-4 from National Research Council Canada).

System	*Agilent 7500 ce*
Reaction cell	Octopole Reaction System
Carrier Gas	Argon (Flow rate = 0.98 l/min)
Make up Gas	Argon (Flow rate = 0.26 l/min)
Reaction Gas	Hydrogen (mode 1) (Flow rate = 5.5 ml/min)
Collision Gas	Helium (mode 2) (Flow rate = 4.2 ml/min)
Matrix	2% HNO_3 – 0.5% HCl. Both produced from triple distilled Aristar products
Tuning solution	Agilent Tuning Solution 10ppb containing Li, Y, Ce, Tl and Co Part # 5184-3566 Its in 2% Nitric Acid and 0.5% HCl
Internal Standards	Scandium (20 ppb), Rhodium (20 ppb), Bismuth (20 ppb)
Sample uptake	Autosampler
Sample volume	1 – 5 ml
Sample introduction to the plasma	Micromist low-flow concentrtic nebulizer
Analysis time	Approximately 60 seconds. Sample uptake time including rinses, tuning solutions, etc. is approximately 5 minutes.

Software for instrument control, data management and quantification	Chemstation

Table 4-12: Technical characteristics of the 7500 ce system.

The analysis mode for each element is presented in Table 4-13.

Element	Mass	Gas	Isobaric interferences	molecular interferences
Na	23	He		
Mg	24	H_2		
Al	27	He		
K	39	He	^{38}ArH	
Ca	43	H_2		
Ca	44	H_2	$^{12}C^{16}O^{16}O$	
Mn	55	He	$^{40}Ar^{14}NH$	
Fe	56	H_2		^{40}ArO, ^{40}CaO
Ni	60	He		$^{43}CaOH$, ^{44}CaO
Cu	63	He		$^{46}CaOH$,$^{40}ArNa$
Zn	66	He		
As	75	He		
U	238	He		

Table 4-13: Analysis mode for analytes on crICP-MS. Interferences are obtained from Horlick and Montaser (1998).

4.4.2 Sample preparation

All the samples that were analyzed on crICP-MS were preserved with 1- 2% HNO_3 (*in-situ* acid addition). All manual samples were filtered through 0.45 μm cellulose nitrate filters. Osmo samples from the first deployments were filtered through the same filters, but during the process some of the sample was lost (dead volumes in the filtration apparatus). Therefore, it was decided not to filter osmo samples. Further dilution depended on the matrix of the samples and on the analytes of interest. Preparation of the samples according to their type is presented in sections 4.4.2.1 and 4.4.2.2.

4.4.2.1 River water samples

For the determination of major cations, all the river water samples were diluted at least 10 fold, in order to bring the concentration of the analytes within the upper concentration limit of the method. For trace metals it is preferable for river water samples to be undiluted, otherwise signals for some trace metals might be close to the detection limit or below that. Dilutions were volumetric, so an

error of ±0.5%, associated with the pipettes is expected. The error that is introduced from the 10 fold dilution of the samples can be evaluated from the measurements of the 10 fold diluted SLRS-4 samples.

4.4.2.2 Sea water samples

Analysis of sea water samples, even by crICP-MS, is challenging. The saline matrix, apart from the polyatomic and isobaric interferences, affects the mechanical parts of the system (nebulizers, sample and skimmer cones), as salts gradually attach on their surface and eventually clog them. For this reason sea water samples need to be diluted extensively. For determination of major cations samples were diluted 5000 fold. With such dilutions trace metal concentrations were much lower than the detection limit. For this reason samples were diluted 20 fold. With such dilutions most trace metal concentrations were detectable, but the precision and accuracy of the method was reduced due to the high salt concentration of samples (deposition of salts on skimmer and sample cones).

4.4.3 System Performance

Evaluation of the crICP-MS system's performance includes the determination of the precision and accuracy (errors), determination of the detection limits, calibration data and also comparison of major cations results, between the crICP-MS system (Agilent® 7500 ce) and the IC (DIONEX® DX500).

4.4.3.1 Precision and Accuracy

Precision and accuracy were determined by analyzing a certified reference material (SLRS-4 CRM from National Research Council Canada). Results are presented in Table 4-14, Table 4-15 and Table 4-16.

Significance tests (one sample t-test) for the above results indicate that a systematic error is present for most analytes and especially for trace metals, which reflects the method's accuracy. Zinc errors are high so results for zinc are not considered reliable. The 1:10 dilutions reduce both accuracy and precision. The RSDs presented in Table 4-14, Table 4-15 and Table 4-16 can be considered as the errors for the method for river water samples.

Results of seawater reference material (CASS-4) were not accurate, so results from seawater samples can only be used for relative comparisons.

Sample	Measurements (mg/l)				
	^{23}Na	^{24}Mg	^{39}K	^{43}Ca	^{44}Ca
SLRS - 4 Dilution 1:10	1.74	1.34	0.54	5.62	5.79
	1.86	1.42	0.65	5.53	5.85
	2.07	1.43	*1.02*	5.64	5.82
	1.82	1.45	0.62	5.71	5.98
	1.97	1.46	0.72	5.49	5.45
	1.99	1.48	0.75	5.53	5.43
	1.84	1.42	0.76	5.73	5.47
Mean (mg/l)	1.90	1.43	0.67	5.61	5.68
σ (mg/l)	0.12	0.04	0.09	0.09	0.23
RSD	6%	3%	13%	2%	4%
Certified value (mg/l)	2.4±0.2	1.6±0.1	0.68±0.02	6.2±0.2	6.2±0.2

Table 4-14: Precision and accuracy for major cations on the crICP-MS. The certified material was diluted 10 fold to evaluate the effect of dilution on the river water samples. The red – italic value was considered an outlier (>2σ from the mean) and was not included in calculations.

Sample	Measurements (mg/l)				
	^{23}Na	^{24}Mg	^{39}K	^{43}Ca	^{44}Ca
SLRS - 4	2.27	1.80	0.66	5.97	5.98
	2.31	1.84	0.68	5.98	5.96
	2.29	1.83	0.68	6.04	6.03
	2.28	1.81	0.67	5.97	5.96
	2.26	1.79	0.67	5.93	5.95
	2.27	1.79	0.67	5.83	5.83
Mean (mg/l)	2.28	1.81	0.67	5.95	5.95
σ (mg/l)	0.02	0.02	0.01	0.07	0.06
RSD	1%	1%	1%	1%	1%
Certified value (mg/l)	2.4±0.2	1.6±0.1	0.68±0.02	6.2±0.2	6.2±0.2

Table 4-15: Undiluted CRM results, which show the improvement in the methods precision and accuracy for major cations.

Sample	^{55}Mn	^{56}Fe	^{60}Ni	^{63}Cu	^{66}Zn	^{75}As	^{238}U
SLRS - 4	3.49	86.96	0.60	1.45	0.35	0.35	0.06
	3.48	85.18	0.59	1.43	0.26	0.31	0.06
	3.47	85.07	0.54	1.50	0.19	0.35	0.06
	3.46	84.37	0.56	1.39	0.23	0.27	0.06
	3.44	86.55	0.58	1.81	0.41	0.32	0.06
	3.44	85.30	0.60	1.42	0.20	0.41	0.06
Mean (mg/l)	3.46	85.57	0.58	1.50	0.27	0.34	0.06
σ (mg/l)	0.02	0.98	0.02	0.15	0.09	0.05	0.00
RSD	0.6%	1.1%	3.9%	10.3%	32.2%	13.6%	4.4%
CRM (mg/l)	3.37±0.18	103±5	0.67±0.08	1.81±0.08	0.93±0.1	0.68±0.06	0.05±0.003

Table 4-16: Precision and accuracy for trace metals with the crICP-MS. Concentrations are in µg/l.

4.4.3.2 Detection – Quantification Limits

The detection limit (LLD as defined in section 4.3.3.2) for each analyte for the crICP-MS method, can be calculated from equation 4-3, which is common practice for many analytical methods.

$$LLD = 3 \cdot \sigma_0 \qquad \textbf{4-3}$$

where σ_0 is the standard deviation blank samples. Results are presented in Table 4-17 and Table 4-18.

	^{23}Na (µg/l)	^{24}Mg (µg/l)	^{39}K (µg/l)	^{43}Ca (µg/l)	^{44}Ca (µg/l)
Blanks 2% HNO_3 & 0.5% HCl	186.6	0.10	0.03	36.68	0.17
	161.5	0.13	0.06	36.05	0.09
	160.3	0.11	0.05	36.44	0.07
	158.8	0.18	0.04	35.76	0.09
	159.4	0.11	0.03	35.42	0.09
	156.7	0.09	0.04	38.26	0.08
	164.3	0.59	0.28	39.86	0.17
	165.5	0.52	0.19	41.76	0.19
	162.9	0.38	0.07	40.85	0.13
	166.7	0.30	0.13	42.02	0.09
	155.5	0.17	0.11	38.83	0.12
σ_0 (µg/l)	8.4	0.18	0.08	2.47	0.04
$3\sigma_0$ = LLD (µg/l)	25.3	0.54	0.24	7.4	0.13

Table 4-17: Agilent 7500ce crICP-MS LLD for major cations.

	^{55}Mn (μg/l)	^{56}Fe (μg/l)	^{60}Ni (μg/l)	^{63}Cu (μg/l)	^{66}Zn (μg/l)	^{75}As (μg/l)	^{238}U (μg/l)
Blanks 2% HNO_3 & 0.5% HCl	0.11	7.89	0.05	1.77	0.62	0.03	0.07
	0.07	37.86	0.18	1.88	0.58	0.00	0.32
	0.13	21.22	0.14	2.79	0.66	0.04	0.12
	0.10	24.00	0.08	1.39	0.63	0.02	0.21
	0.03	17.48	0.16	1.91	0.70	0.03	0.06
	0.10	20.13	32.80	5.92	0.72	0.03	0.17
	0.18	42.16	0.49	11.53	1.94	0.03	0.17
	0.11	51.77	0.44	5.16	1.61	0.06	0.09
	0.16	37.98	0.23	4.51	1.10	0.03	0.13
	0.16	32.03	0.35	5.81	0.98	0.01	0.17
	0.08	60.64	0.32	2.24	0.83	0.03	0.29
σ_0 (μg/l)	0.04	15.80	9.82	3.01	0.45	0.02	0.08
$3\sigma_0$ = LLD (μg/l)	0.13	47.41	29.45	9.02	1.35	0.05	0.25

Table 4-18: Agilent 7500ce crICP-MS, detection limits for trace metals.

From Table 4-17 it is evident that blanks of Na and ^{43}Ca present higher concentrations than blanks of the other analytes – 0.15 mg/l for Na and 0.04 mg/l for ^{43}Ca. These blank concentrations were considered acceptable as the concentrations of these analytes in the collected samples (both river water and sea water) will be at least an order of magnitude higher than the above values. Moreover the sensitivity of the method, for all analytes is sufficient to identify concentration differences of the collected samples.

4.4.3.3 Calibrations

All calibrations were linear (type y = ax+b). The concentration range for the calibrations depended on the type of samples and the type of analytes. For river water samples the calibration range for major cations was from 1 μg/l to 8000 μg/l and for trace metals it was from 0.1 μg/l to 20 μg/l. For most analytes the high dynamic range of the calibrations did not affect linearity.

Calibration results are presented in Table 4-19.

Analyte	Type	Points	Concentration of Standards (μg/l)	Cor. Coef.
^{23}Na	Linear	7	50 – 100 – 500 – 1000- 2000 – 4000 – 8000	0.9997
^{24}Mg	Linear	6	10 – 50 – 100 – 500 – 1000 – 2000	0.9999
^{39}K	Linear	7	50 – 100 – 500 – 1000- 2000 – 4000 – 8000	0.9999
^{43}Ca	Linear	4	100 – 500 – 1000 – 2000	0.9999
^{44}Ca	Linear	5	50 – 100 – 500 – 1000 – 2000	0.9997
^{52}Mn	Linear	5	0.1 – 0.5 – 1 – 5 – 10 – 20	0.9999
^{56}Fe	Linear	4	1 – 5 – 10 – 20	0.9998
^{60}Ni	Linear	7	0.01 – 0.1 – 0.5 – 1 – 5 – 10 – 20	0.9999
^{63}Cu	Linear	6	0.1 – 0.5 – 1 – 5 – 10 – 20	0.9999
^{66}Zn	Linear	5	0.5 – 1 – 5 – 10 – 20	0.9998
^{75}As	Linear	6	0.1 – 0.5 – 1 – 5 – 10 – 20	0.9999
^{111}Cd	Linear	6	0.1 – 0.5 – 1 – 5 – 10 – 20	0.9999
^{238}U	Linear	6	0.1 – 0.5 – 1 – 5 – 10 – 20	0.9999

Table 4-19: Calibration for crICP-MS for river and seawater samples.

4.4.3.4 Comparison between crICP-MS and IC

The comparison principles are the same as the ones that were used to compare the two IC systems (section 4.3.3.4). For this comparison we assume that the IC system is more accurate, a fact that is demonstrated by the measurements of the reference materials for each method. Moreover, IC is an established method for the determination of major cations in environmental waters, while determination of major cations with ICP-MS is still under development. Results from the comparison of the two systems are presented in Figure 4-2 and Table 4-20.

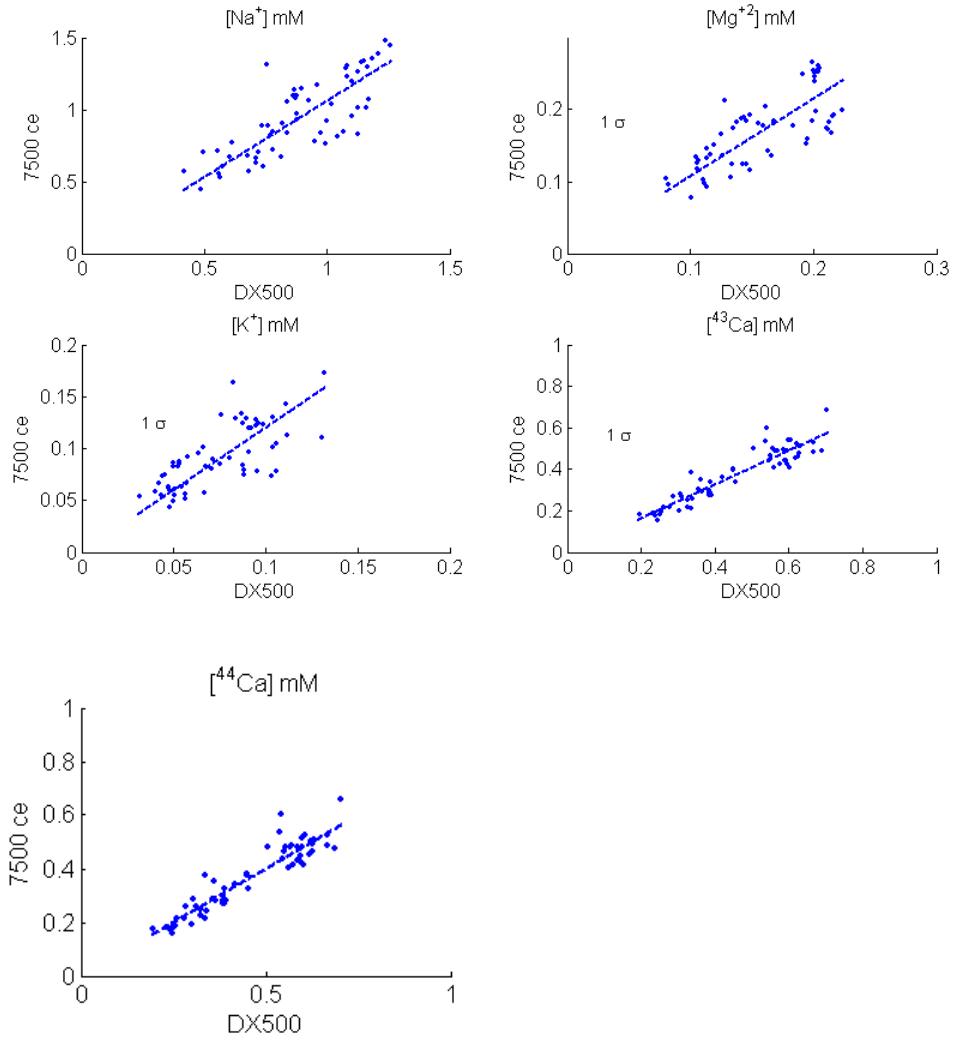


Figure 4-2: Comparison between crICP-MS and IC. Data are from the one month deployment of the SCAWS and includes both manual and osmo samples.

Parameters (95% confidence level)		DX500 vs Agilent 7500 ce				
		Na^{+}	K^{+}	Mg^{+2}	$^{43}Ca^{+2}$	$^{44}Ca^{+2}$
y = ax	slope (a)	1.01	1.24	1.048	0.815	0.798
	R^2	0.62	0.46	0.56	0.86	0.87
y=ax+b	slope (a)	0.97	0.89	0.94	0.82	0.81
	intercept (b)	0.084	0.025	0.024	-0.0034	-0.0057
	R^2	0.62	0.53	0.56	0.86	0.86

Table 4-20: Results from the regression analysis between crICP-MS and IC for major cations.

Results from the 1:1 comparison indicate that the correlation coefficients are low, which may be related to lowest precision of the crICP-MS comparing to the IC. Nevertheless, the slopes for both linear models and intercepts are close to 1 and 0 respectively. This indicates that systematic errors

of the calibrations and of the calculations of the background signal are minimized. However the results are encouraging, indicating that determination of major cations with crICP-MS (at least for river water samples) is reliable.

4.5 Additional Methods

Additional methods include, determination of total alkalinity with the end-point titration method (Eaton *et al.*, 2005), determination of nutrients in seawater samples using standard analytical techniques (Morris and Riley, 1963) and measurement of total suspended solids (Eaton *et al.*, 2005). These parameters were measured only on manually collected river water samples, in order to gain a more complete picture of the river chemistry during the deployment period. Measuring alkalinity in the SCAWS samples is possible with a method that requires a very small amount of sample. The main requirements for this method is a pH microelectrode (e.g Unisense pH microelectrode), which has a very fine tip and can measure pH in small sample volumes. Equally important is to have a micro burette able to dispense nl. Such equipment was not available for this project.

4.5.1 Total Alkalinity

The importance of alkalinity in natural waters has been demonstrated extensively in the literature (Drever, 1988; Stumm and Morgan, 1996). For this project alkalinity values were essential in order to get a holistic picture of the changes in water chemistry, during the deployment period of the SCAWS. Standard methods for the determination of alkalinity include the Inflection Point Titration, the Gran plot method and the End-Point titration method. The end-point titration method was used, which for our samples did not have significant differences from the Gran method.

The equipment used for the measurements was:

Acid:	PROLABO® HCl 0.1001 N Titrinorm solution
pH electrode:	Fisher® FB68792
pH meter:	Orion® Research EA920 Expandable Ion Analyzer (±0.01 of pH unit)
Acid dispenser:	Brand® Microdispensing pipette HANDY STEP (increments of 12.5 µL/dispense ± 0.1 µL)
	Schott® Titronic 96 digital titrator (0.01 ml/dispense ± 15%)
Stirrer:	Teflon coated magnetic bar

According to the method the end point pH for total alkalinity, should be between 4.3 – 4.7 as in this pH region the bicarbonate ions (HCO_3^-) are in equilibrium with carbonic acid (H_2CO_3). It was decided to calculate total alkalinity at pH = 4.5.

As far as it concerns treatment of the samples before the analysis, the Standard Methods for the Examination of Water and Wastewater (Eaton *et al.*, 2005), suggests that the samples should not be treated e.g. diluted or filtered. The method though that the United States Geological Society (USGS) has issued, recommends the samples to be filtered through a 0.45 μm pore size filter, so that particulates that might consume acid, and contribute to total alkalinity, are removed. Measurements on both filtered and unfiltered sample did not show differences above the error of the method. Even so, it was decided to filter samples (0.45 μm cellulose nitrate filters), so that particulates are removed.

4.5.1.1 Evaluation of the method

To evaluate how accurate and precise the method is we measured the alkalinity of a reference sample and conducted replicate analysis on some samples. Results are presented in Table 4-21. The degree of accuracy and precision of the method are acceptable for the purposes of this study. As will be presented in chapter 6, the method responded well to changes in alkalinity of the samples.

	Total Alkalinity at pH = 4.5 (meq HCO_3^-/l)	Theoretical Value (meq HCO_3^-/l)
Sample 1	2.25	2.21
Sample 2	2.27	
Sample 3	2.25	
Average	2.26	
σ	0.014	
RSD (%)	0.6	
Bias	0.05	
Precision	0.06	

Table 4-21: Accuracy of total alkalinity method.

4.5.2 Determination of Nutrients in Seawater

The limitations of ion chromatography for the determination of nitrate and phosphate were explained in section 4.3.2.2. In the same section it was explained why samples from the SCAWS could not be analyzed for nutrients using standard analytical seawater techniques (coloured samples from tracer injection). Manual samples though could be analyzed for nutrients using a standard method (Morris and Riley, 1963). This analysis can be used to evaluate the performance of the ion chromatography system for the determination of nitrate in saline samples and at low concentrations, and at the same time gain a more precise picture of the nutrient distribution during sampling periods.

Samples were analyzed with a "Skalar San++ segmented flow auto – analyzer". The analytical protocol follows Kirkwood's method (Kirkwood, 1996). Samples are analyzed simultaneously for nitrate, phosphate and silicates. Detection limits are 0.2 μM, 0.04 μM and 0.06 μM respectively. Calibrations were linear for all three analytes. The calibration range was from 0.5 μM to 10 μM, for all analytes, and linearity was not affected by this range difference. Higher calibration ranges did affect linearity, and for this reason samples needed a 10 fold dilution (volumetric), in order to bring nitrate and silicate concentrations within this range. Silicate concentrations of undiluted samples were up to 20 μM, and their values could be extrapolated linearly from the calibration curve. Relative errors for all three analytes are ± 1%. The contribution (error) of dilution can be estimated from the silicate undiluted and diluted values. The error is ±4% (see APPENDIX for data and calculations).

4.5.2.1 Comparison between the Autoanalyzer and Ion Chromatography

Results from the two methods of manually collected seawater samples (NOCS floating pontoon) are presented in Figure 4-3.

The results highlight the differences between the two methods. For most samples the differences are higher than the errors of both methods. Assuming that results from the autoanalyzer are more precise and accurate, ion chromatography results for nitrate concentrations of all seawater samples are ambiguous.

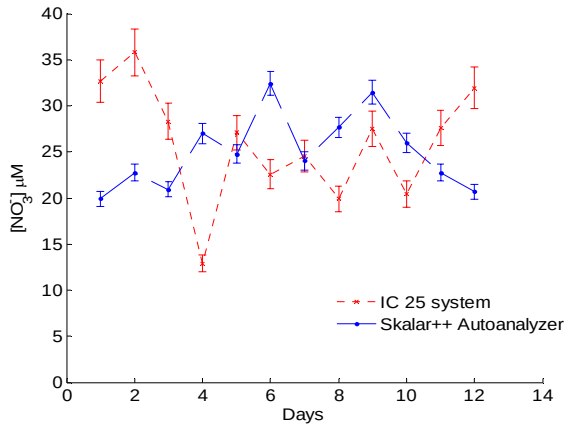


Figure 4-3: Nutrient autoanalyzer and IC25 comparison. For the IC25 system, errors were calculated from the nitrate RSD (7%) as presented in Table 4-6. For the Skallar++ autoanalyser errors were calculated based on the dilution error (4%).

4.5.3 Total Suspended Solids

Determination of suspended solids was necessary for the evaluation of the SCAWS's filtering system (section 3.3.3). Suspended solids were also measured on manually collected samples during the one month river deployment.

We used the method that is proposed in Standard Methods for the Examination of Water and Wastewater (AWWA (Eaton *et al.*, 2005)). The method is based on the filtration of a known amount of water through a pre-weighted glass fibre filter (GFF), drying of the filter until constant weight at 105 ^{o}C (±1 ^{o}C) and weighing of the filter again. The weight difference of the filter normalized to the sample volumes gives an estimate of the samples suspended solids co0ncentration. Evaluation of the method's accuracy is not feasible as reference materials for this method are not available. Indicative numbers of the performance (reproducibility of measurements) of the method are presented in Table 4-22.

Sample	SS of tap water with resuspended sediment (mg/l)	River Water sample 18/05/08 (mg/l)
1	3.7	5.66
2	3.9	6.34

Table 4-22: Reproducibility of total suspended solids determination method.

4.6 Conclusions

The basic requirement from the analytical methods was to have the necessary resolution in order to identify changes in concentrations of analytes, both for river water samples and seawater samples. The sample preparation and analysis protocols that were chosen indicate that both ion chromatography and crICP-MS can deliver that.

The two ion chromatography systems that were used (IC25 and DX500) produced reliable data even with small amounts of sample volumes, which is very critical for the SCAWS. Ion chromatography systems performed very well on river water samples. For analysis of conservative elements (Na^{+}, Cl^{-}, Mg^{+2}, Ca^{+2}, SO_4^{-2}, Br^{-}) in seawater samples the extensive dilutions (e.g. 2000 fold dilutions) that are required in order to bring the concentration within the range of the instruments yield errors (RSD) of 4%. The systems however do not produce reliable results for nitrate in seawater as the nitrate concentrations, after 500 fold dilution, reach (or even go below) the methods detection limit (0.16 μM).

Collision reaction ICP-MS was also reliable for the analysis of river water samples. The RSD for Na is 6% and for the rest of the major ions is less than 2%. For trace metals RSD can be as high as 10%. Technical difficulties did not allow for use of the High Matrix Induction system that allows

analysis of seawater samples without the need to dilute the sample extensively (10 fold dilution instead of a 2000 one).

Overall, as will be presented in chapters 5 and 6, the analytical methods were able to give a realistic picture of the analysed samples. This was essential in order to evaluate the performance of the SCAWS.

5 SCAWS marine deployments

5.1 Rationale

After the development of the first prototype (MK I) and the completion of the initial lab tests, it was necessary to test the sampler's performance in a natural environment. The tests aims were to evaluate the following:

- Ability of the device to sample in natural environments
- Performance of the time stamping – tracer addition system
- Performance of the filtering system.

External power supply and frequent monitoring of the sampler's performance were necessary for these tests. For these reasons the first test deployments (in a natural environment) took place in NOCS floating pontoon (Southampton Water), so we were able to monitor the sampler regularly.

The sampling performance and the ability of the sampler to collect representative samples, was evaluated by comparing concentrations of various analytes between the SCAWS samples and manual samples that were collected from the same sampling site during deployments.

Before the marine deployments, the SCAWS MKI prototype was deployed in the NOCS acoustics tank for a period of five days, in order to identify any mechanical problems while the sampler is submerged. During the deployment the sampler's mechanical performance was good and all parts operated properly. The successful deployment in the acoustics tank set the ground for a deployment in NOCS floating pontoon.

The SCAWS has been deployed three times in NOCS floating pontoon. The first deployment lasted for one week, the second for 5 days (short term deployments), and the third was for 12 days (mid term deployment)

5.2 Setting

NOCS floating pontoon is located in Southampton Water (see Figure 5-1). Southampton Water is an estuary stretching from the Solent up to Southampton area, where the rivers Itchen and Test discharge (combined average annual discharge of the rivers is 1.5×10^6 m^3/d (Hydes, 2000)). The estuary is 10 km long, the widest point is 2.5 km and the deepest point is 10 m. The intense development of the area over the past 50 years and the importance of the estuary on social and economical development, led to detailed and extensive studies of its geological, physical and biochemical characteristics (Burton, 1980; Collins and Ansell, 2000).

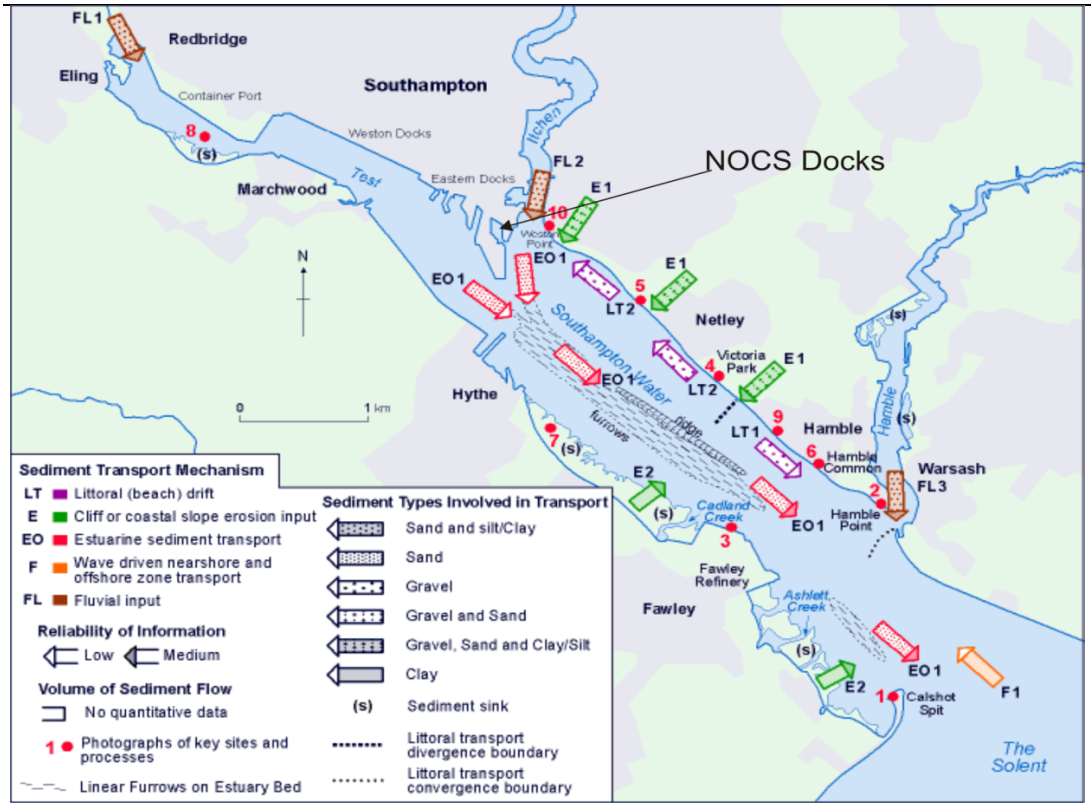


Figure 5-1: Southampton water sediment transport.
http://stream.port.ac.uk/environment/scopac5/soton/index.htm.

The estuary is considered macrotidal with a mean tidal range of 4.5 m, and experiences both tidal and residual (non – tidal) currents (Sharples, 2000). Studies of spatial and temporal distributions of nutrients (Hydes and Wright, 1999; Hydes, 2000) and trace metals (Fang, 1995; Statham, 2000) in the estuary (see Table 5-1), demonstrate the effect of the above mentioned physical parameters on the residence time and pathways of chemical substances. More specifically Hydes et al, (1999), report that diurnal differences in salinity can be up to 4 psu. Measurements of nitrate between August and October 1996 are indicative of the tidal effects on nitrate. During this period a change of 4 psu in salinity (31 – 35 psu), was associated with a 40 μM change in nitrate concentration. Based on the conservative behaviour of nitrate, in Southampton Water it is expected that other conservative analytes will present similar diurnal variations.

Concerning the NOCS docks micro-environment, the annual variability of temperature, salinity, nutrients and phytoplankton were studied by Altisan (2006). In this study data were collected every week during 2002. Diurnal changes, within this micro environment have not been studied. An important feature of the area is the maritime and industrial activity within the docks (vessel berth, movement, industrial activities) which is more than likely to affect the marine environment, and especially concentration of chemical substances (e.g. cooling water from docked ships, small spillages, etc).

Monitoring and studying this marine microenvironment is not the purpose of this study, instead the collected data will be used within the context of the SCAWS performance evaluation. However all data will be evaluated relative to any available past information.

Salinity Range	32.1 - 34.4
Trace Metals (nM)	
Cd	0.10-0.54
Co	0.63-2.80
Cu	9.6-22.5
Fe	8.0-109
Mn	8.7-75.0
Ni	6.7-28.6
Pb	0.11-0.66
Zn	9.4-48.0

Table 5-1: Concentration (nM) range of some dissolved trace metals in Southampton Water (Statham, 2000).

5.3 Short term marine deployments

5.3.1 First marine deployment

The first deployment of the SCAWS in NOCS floating pontoon was for one week (23/04/2007 – 30/04/2007). The sampling tube was 20 m long, the micro-solenoid pump was set to operate daily and the filtering system was set to operate every three days. During the deployment period manual samples were collected during high and low tide, in order to identify how much analytes concentrations vary with tides.

After the sampler was recovered it was evident that even though sampling was continuous (that was evident from the progression of the first rhodamine strip) the tracer injection system did not operate properly. There should have been seven rhodamine strips in the sampling tube and instead there were five. This indicated that the electronics did not operate properly. Examination in the lab indicated that there was a problem with the internal clock of the PIC microcontroller, which was tackled efficiently. The malfunction of the tracer addition system, did not allow for the accurate segmentation of the sampling tube. Therefore the samples from the SCAWS were not representative. Samples were analyzed only for major anions on the IC25 system. Results are presented in Table 5-2.

The results indicate the poor performance of the sampler during this deployment, as there are significant differences on the results between the two sampling methods.

In addition to the malfunction of the tracer addition system, the filtering system did not operate as well. This was evident by the fact that a mark on the nylon mesh was found on the same spot after recovery of the sample. The malfunction of the filtering device might be related to the electronic circuit, but what was evident after recovery was that the renewing mechanism was not aligned properly (probably due to movement of the sampler in the water). Therefore, even if the electronics had operated properly, the friction on the magnets and the worm-gear mechanism was such that the stepper motor could not rotate and move the filter. The solution to this problem has been discussed in sections 3.2.4 and 3.3.4.2. It should be noted that the malfunction of the filtering system did not affect uptake of water into the sampling tube.

All the above clearly indicated that the first prototype needed improvements in many aspects in order to perform reliably in natural environments.

	Cl^- (mM)		Br^- (mM)		SO_4^{-2} (mM)	
	Manual	SCAWS	Manual	SCAWS	Manual	SCAWS
1	509.9	416.7	0.55	0.49	23.4	17.0
2	496.3	469.1	0.54	0.53	22.8	22.0
3	549.2	474.7	0.60	0.56	25.4	22.6
4	565.2	501.6	0.61	0.57	26.1	23.1
5	546.7	528.5	0.61	0.60	25.5	24.2
6	551.7		0.61		25.7	
7	555.2		0.63		26.2	

Table 5-2: Results from the 1st marine deployment in NOCS docks. Samples were analyzed on the IC25 system. Data of manual samples is the average concentration between low tide and high tide samples. All results are presented in the APPENDIX.

5.3.2 Second marine deployment

The first deployment of the MKI prototype highlighted certain problems of the sampler's performance. The most important one was the unstable operation of the electronic circuit, which affects the operation of the tracer injection system and of the cassette filter renewing mechanism (stepper motor). The problem was rectified and tests in the laboratory, confirmed the stable operation of the system.

For the filtering system, further tests in the laboratory proved that any misalignment will compromise its operation. This is more than likely to occur when the sampler is deployed in a natural marine environment, where water motion can be vigorous (waves, tides, currents).

The SCAWS was redeployed in NOCS docks from 26/05/2007 to 30/05/2007. The sampler was equipped with a 20 m sampling tube, and instead of the cassette filter it was equipped with a 0.45 μm polysterene on-line filter. The rationale behind its use was to protect the sampling tube from

aggregate material that might enter into it and block it, and at the same make it easier to prepare the SCAWS samples for analysis without requiring further filtration (see section 3.3.3).

An important issue that came up from the first deployment was that in case the tracer addition system does not operate properly, sampling resolution is ambiguous and samples are not representative. For this reason it was decided to record the temperature during the deployment and from the temperature – flow rate relationship, deduce the daily flow rate and segment the tube accordingly (see section 3.3.1). Temperature was recorded with the YSI 6600 water monitoring system (https://www.ysi.com, see APPENDIX for technical details) that records temperature, depth, salinity, pH, chlorophyll and dissolved oxygen. The YSI 6600 was set to collect data every hour and only temperature and salinity data are presented.

Manual samples were also collected during the deployment period (low tide and high tide) both for ion chromatography and crICP-MS analysis (see sections 4.3.2.2 and 4.4.2.1 for sample preparation and treatment).

5.3.2.1 Results

In this deployment the tracer injection system performed well, as the rhodamine strips were discrete and their number matched the deployment days. After recovery the sampling tube was segmented according to the rhodamine strips which matched the segmentation profile that is produced from the temperature – flow rate relationship (Table 5-3).

Date	Temperature (^{o}C)	Flow rate (ml/d)	Theoretical length (cm)	Rhodamine length (cm)
26/05/2007	15.9	1.32	168	172
27/05/2007	15.7	1.30	166	168
28/05/2007	15.3	1.28	163	170
29/05/2007	14.9	1.26	160	155
30/05/2007	14.8	1.25	159	155

Table 5-3: SCAWS flow rate during the 2nd deployment and sampling tube lengths. Temperature values are averaged from the hourly YSI-6600 measurements.

Temperature and salinity diurnal records during the deployment period are presented in Figure 5-2.

Results from analysis of samples with ion chromatography and crICP-MS are presented in Figure 5-3, Figure 5-4 and Figure 5-5. In these figures the SCAWS samples profiles are presented as step change diagrams. This is to emphasize the fact that the SCAWS is integrating changes that might occur during the sampling resolution (e.g daily) in one sample, while conventional manual sampling provide only a "snapshot" of the environments characteristics. This is a fundamental detail for the SCAWS, which can explain differences of certain analytes concentrations between samples from the two methods.

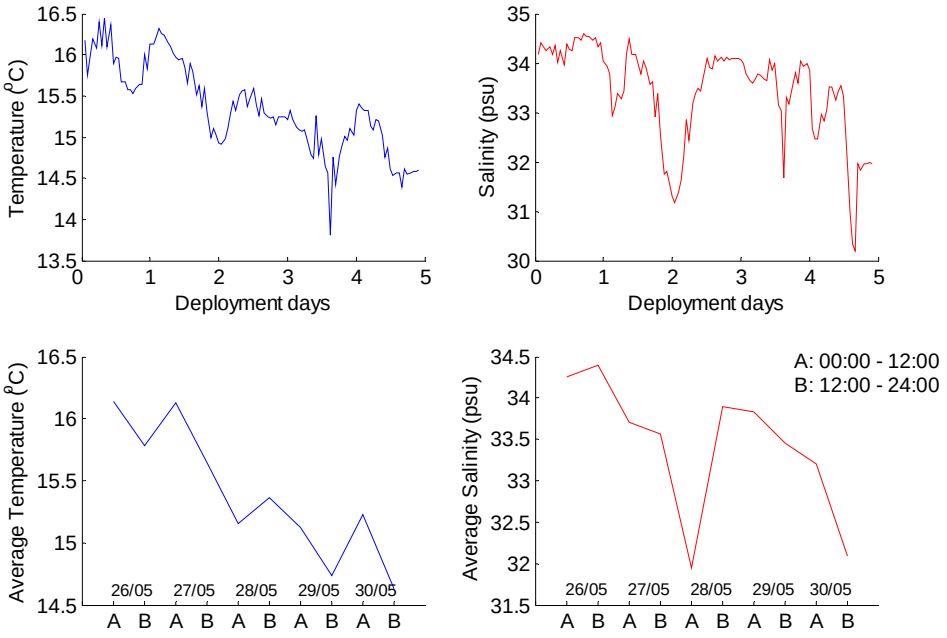


Figure 5-2: Temperature and Salinity diurnal variability during 2nd SCAWS deployment. Data were collected with the YSI-6600 monitoring system. The upper two figures are data collected every hour during the deployment period.

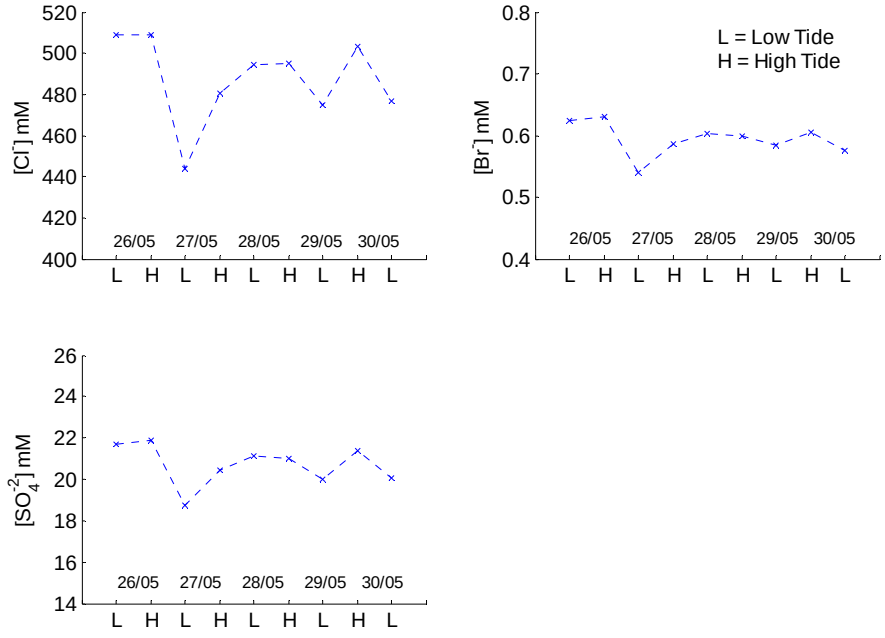


Figure 5-3: Tidal variations of anion concentrations during the 2nd deployment. Data are from manual samples.

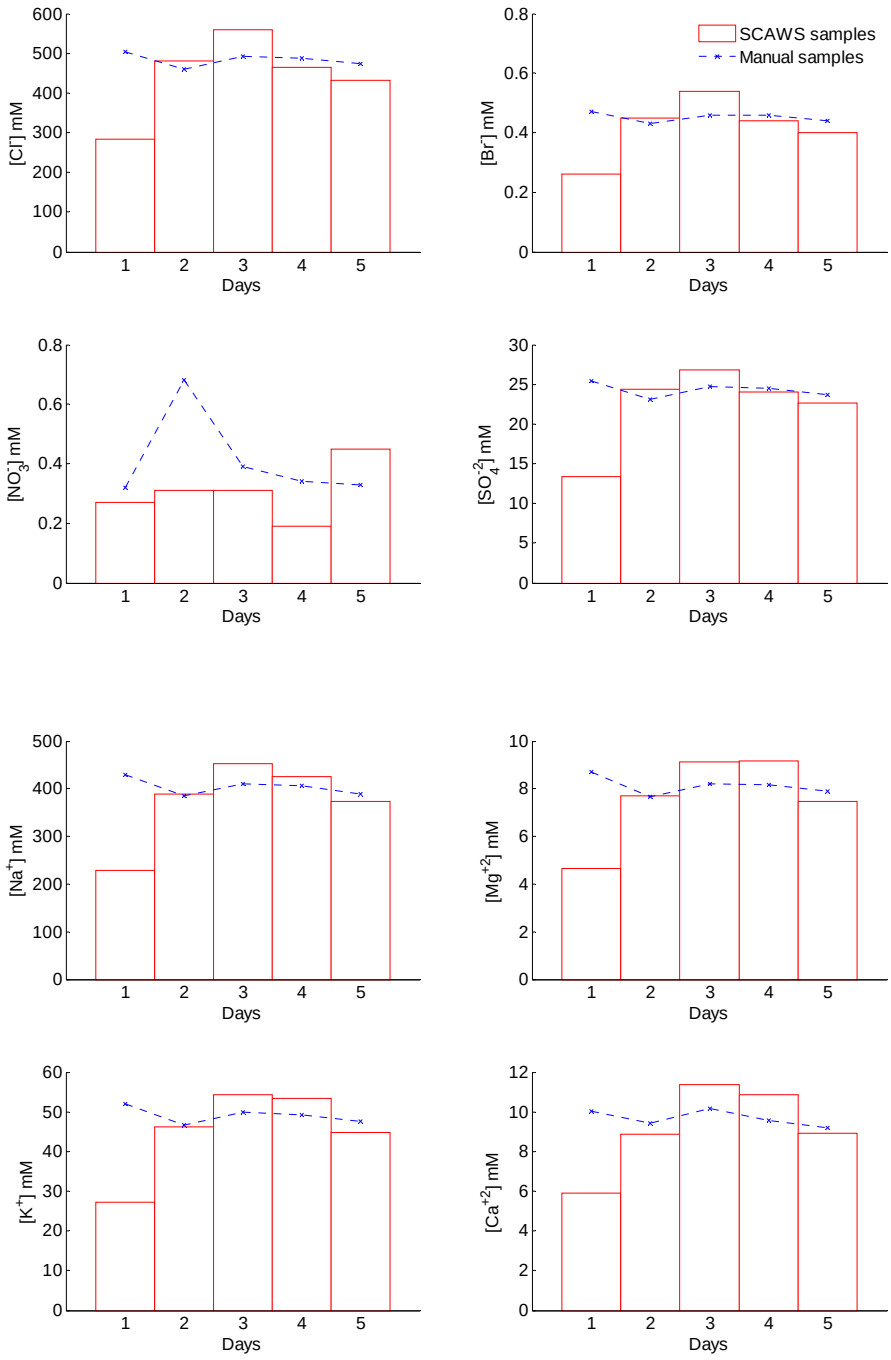


Figure 5-4: Comparison between manual and SCAWS samples for major ions. Anions were determined with the IC25 system, and cations with the Agilent 7500 ce crICP-MS. Data from manual samples are averaged values of the two daily samples that were collected. Nitrate data should not be considered reliable and are presented to compare the sampling methods and identify relative changes.

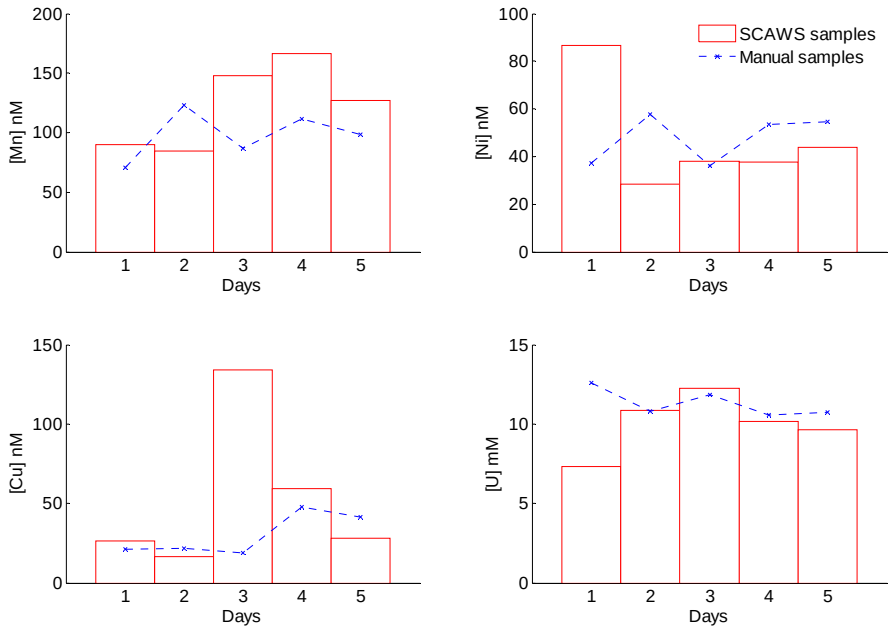


Figure 5-5: Comparison between SCAWS and manual samples for trace metals. Manual samples are averaged from the two tidal samples. Data are used only to identify relative changes.

5.3.2.2 Discussion

In this deployment the mechanical performance of the sampler was improved. Sampling was continuous and undisrupted and the tracer injection system operated well. The fact that the rhodamine strips matched the temperature – flow rate profile was highly encouraging and indicative of the tracer addition –time stamping system's reliability during this deployment.

For all conservative analytes there is a significant difference between the first sample collected from the SCAWS and the first manual sample. This is due to the fact that the first SCAWS segment was cut further in the deionized water part, so the final sample was diluted. The following samples have differences within the errors of the analytical method.

The salinity decrease (from 34 to 31 psu) on the 2nd day is evident on the manual samples profile in all analytes. This is not so clear on the SCAWS samples profile, because of the first samples dilution effect, but the fact that the SCAWS samples profiles "catch up", exactly at that point indicates its good performance. Both the SCAWS samples and the averaged manual samples are integrating the variations that are evident from the salinity profile (Figure 5-2) but also from the tidal variations diagram (Figure 5-3).

Nitrate data are not reliable (see section 4.3.2.2), which is proved by the much higher concentration of the samples (0.1 – 0.4 mM), comparing with data from previous studies (0.02 – 0.08 mM) (Hydes and Wright, 1999; Hydes, 2000; Altisan, 2006). Our data can only represent relative

changes in concentrations, as it is expected analytical errors to be similar for both types of samples (SCAWS – manual). Still results between the two sampling methods are significantly different, indicating the need to improve the analytical technique, but also to consider sampling of sensitive analytes.

Trace metals concentrations follow different pattern than conservative analytes (uranium has a conservative behaviour in seawater). Contamination from the sampler itself should be significantly less than the contamination from the floating pontoons metallic parts, which in addition to the rest of the activity within the NOCS docks create an environment with variable trace metal concentrations. This can be more evident when the results are compared with literature data from the Southampton Water – Solent region (Table 5-1). Trace metal concentration of the collected samples during the five day deployment are three orders of magnitude higher than those in Table 5-1.

5.4 Mid – term marine deployments

After the successful second deployment the MKI SCAWS prototype was deployed twice in NOCS docks for the period of 12 days and two weeks. These are still short periods but they will provide more coherent information on the sampler's performance. Manual samples were collected once a day between 12:00 and 14:00 p.m. The third SCAWS deployment was in August 2007 (16-08-07 to 27-08-07) and the forth was in May 2008 (6-05-08 to 21-05-08). For these deployments the YSI monitoring system was not available. Seawater temperature was recorded with a temperature sensor that was fixed on the floating pontoon, which was connected to a transducer, which in turn was connected on the NOCS local area network so data were recorded on a personal computer (equipment is already installed on the pontoon for other experiments). Seawater temperature was recorded every hour.

The sampling tube length for both deployments was 50 m. The time stamping system, was set to operate every day during the 3rd deployment. For the 4th deployment the system was activated manually every day due to a problem on the data logger (one of the PIC's MOSFETs failed and the repair time was expected to be long).

As far as it concerns the filtering system, the worm – gear design was abandoned, because further tests in the laboratory, where the system was placed in a water bath under vigorous conditions, verified that the system is unstable. By the time of the 3rd deployment the new system has not been manufactured so the same 0.45 μm cartridge filter was used.

5.4.1 Third marine deployment

5.4.1.1 Results

The seawater temperature profile during the deployment period is presented in Figure 5-6, where, as in the 2nd deployment, it is evident that these variations will produce a variable sampling rate.

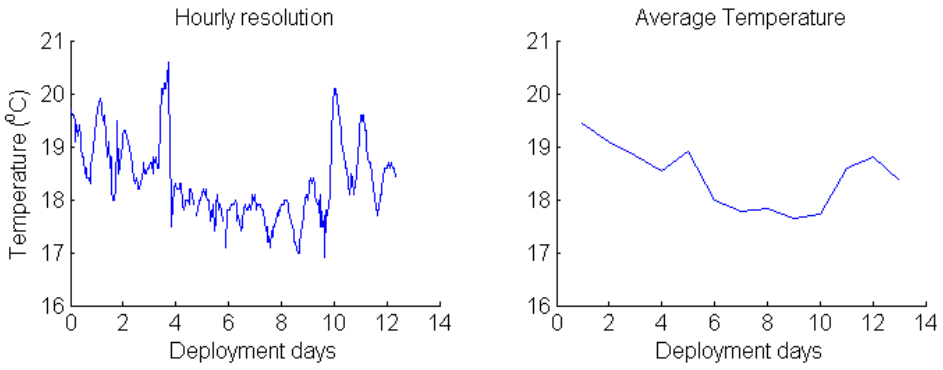


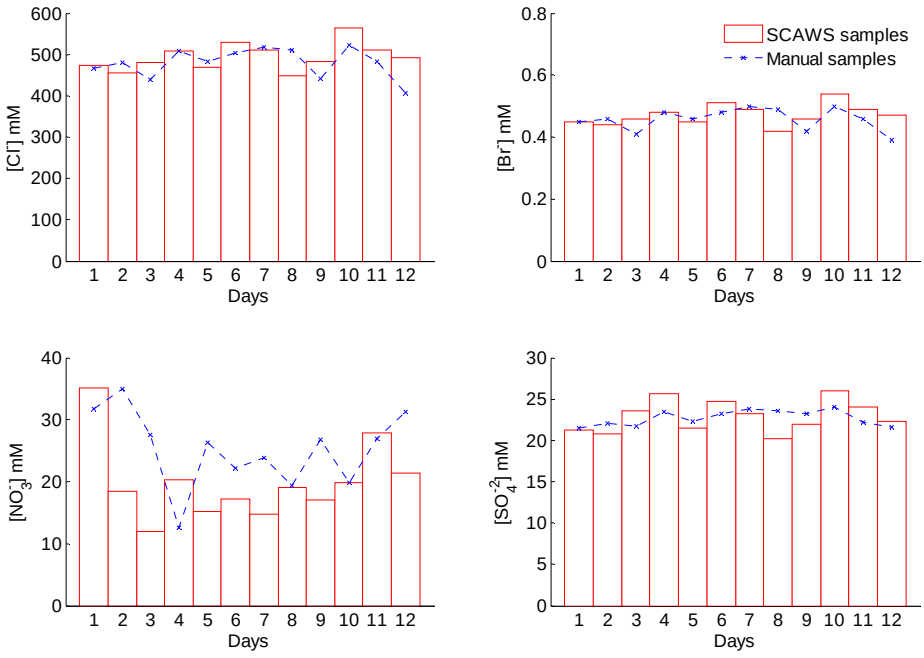
Figure 5-6: Seawater temperature variations during the 3rd deployment. The average temperature profile represents average daily variations.

The recovery and segmentation procedure were similar to the one that was followed on the 3rd deployment. In this deployment the dispersion of rhodamine along the sampling tube was greater than on the previous deployment, but still segments were discrete. As with the previous deployment, the rhodamine segmentation profile was similar (small differences) to that produced from the temperature – flow rate relationship (see Table 5-4).

The concentrations of major ions and trace metals during the 3rd deployment of the SCAWS are presented in Figure 5-7

Date	Temperature (°C)	Flow rate (ml/d)	Theoretical length (cm)	Rhodamine length (cm)
15/08/2007	19.4	1.54	197	201
16/08/2007	19.1	1.52	193	188
17/08/2007	18.8	1.50	191	185
18/08/2007	18.5	1.48	188	194
19/08/2007	18.9	1.51	192	201
20/08/2007	18.0	1.44	184	183
21/08/2007	17.8	1.43	182	179
22/08/2007	17.8	1.43	182	190
23/08/2007	17.6	1.42	181	185
24/08/2007	17.7	1.42	181	174
25/08/2007	18.6	1.48	189	182
26/08/2007	18.8	1.50	191	190
27/08/2007	18.4	1.47	187	179

Table 5-4: SCAWS flow rate during the 3rd marine deployment and sampling tube lengths. Temperature values are averaged from the hourly measurements



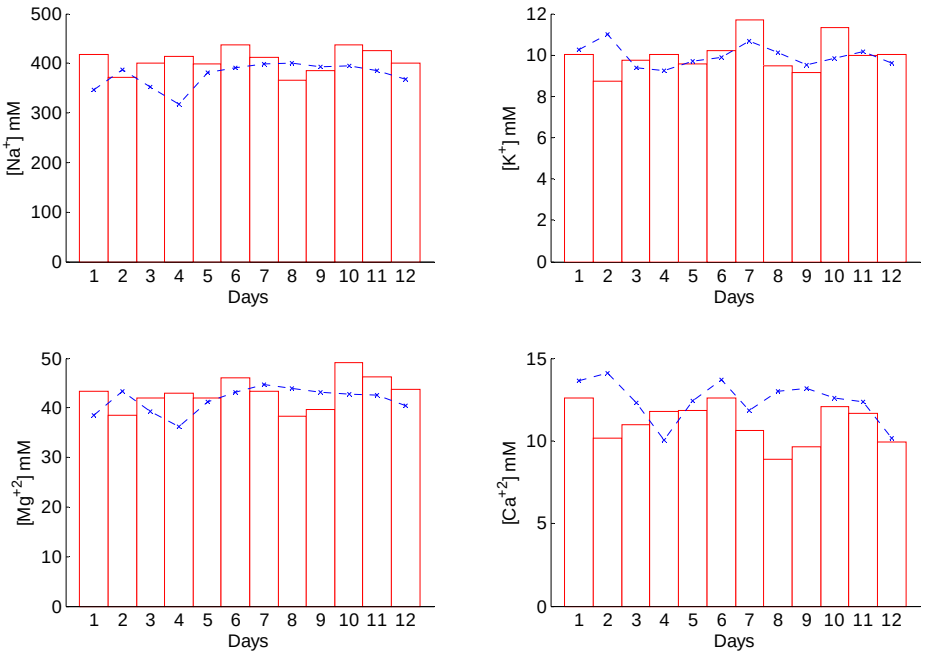


Figure 5-7: Major ions (anions and cations) comparison between SCAWS and manual samples (3rd marine deployment). Cation data are from the DX500 system, anion from the IC25 system.

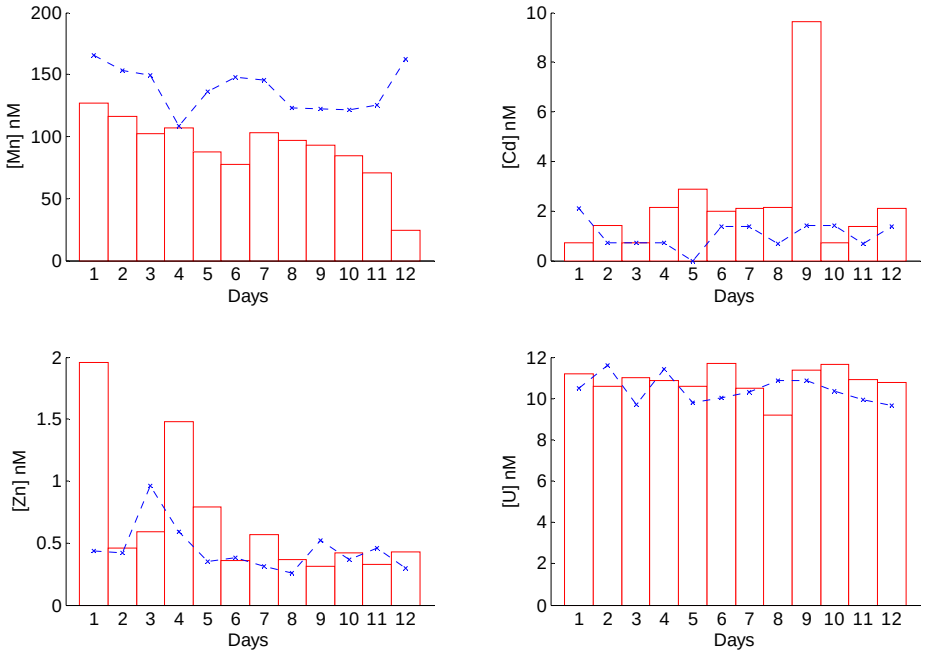


Figure 5-8: Trace metals comparison for SCAWS and manual samples (3rd NOCS deployment).

5.4.1.2 Discussion of results

Overall performance of the sampler was good. The test for the tracer addition system on the 3rd deployment was positive. Injection of rhodamine was consistent and, even though rhodamine dispersion had increased (visual evaluation), the strips were discrete and segmentation was accurate. The cartridge filter was not blocked. A biofouling film and algae were evident on the cartridge, but this did not affect sampling.

The "chemical" performance of the sampler was also good. The first sample was not diluted and the concentration profiles for conservative elements for both sampling methods are similar. There were no indications that the differences were related to any sampling artefacts from either sampling techniques (e.g contamination, SCAWS malfunction). A percentage of the differences can be related to the errors entailed on the analytical methods (see chapter 4). However, the SCAWS samples profiles are more variable than the manual samples. This may be due to the tides, as the manual sampling fails to capture these variations. This demonstrates the difference between a sampler like SCAWS that integrates, and captures, differences over a specific sampling period, and conventional low frequency and discrete sampling methods.

Nitrate concentrations are still significantly different between the two sampling methods (see section 4.5.2), but it is encouraging though is the fact that the changes in concentration follow the same pattern. Also the fact that nitrate concentrations are within the concentration range of literature data, suggests that the data are more realistic.

Trace metal profiles present significant differences (except uranium). This can be related to the absence of a preservative medium (e.g HCl). The importance for preservation has been discussed (section 2.3.3) and results support the need for a preservation addition system for trace metals sampling.

5.5 Review of SCAWS performance in a marine environment

The deployments in NOCS docks were the first and crucial tests for the SCAWS in natural environments. The sampler was subjected to some of the challenges that appear when equipment is deployed and left unattended for a long period of time (changing climatic conditions and changing physical parameters). The two main objectives of these deployments were to evaluate the integrity of the sampler's parts when the sampler operates in a natural environment, and to identify how reliable and representative are the collected samples.

5.5.1 Mechanical performance

The most important test was to establish that the osmo pump can work properly in natural environments. Tests in the laboratory (see chapter 3) have proved that the osmotic pump can

operate underwater, but in a natural marine environment ambient conditions change constantly, which can affect the performance of the sampler (e.g. vibrations from waves and water motion may displace the osmotic pumps and destroy the osmotic gradient). The deployments indicated that the osmo pump can operate in natural environments.

For the innovative parts of the SCAWS, the marine deployments highlighted problems in the original design that have not appeared during tests in the laboratory. The deployments helped to address the following issues:

- Redesign and develop a new mechanism that renews the cassette filter and come up with a more efficient and powerful magnetic coupling.
- The electronics system did not operate consistently on the 1st deployment and it was necessary to rectify the problem (software and hardware issues). At the next two deployments (2nd and 3rd) the tracer addition system performed reliably supporting the fact that the system is useful for the sampler.

The mechanical performance was positive, judging from the fact that the SCAWS managed to collect samples.

5.5.2 "Chemical" performance – Sampling reliability

During all marine deployments, the concentration profiles of conservative elements, for both sampling method were similar. A percentage of these differences is related to the errors that the analytical methods entail (see chapter 4). An interesting fact is that the concentration variations in the SCAWS samples are higher than in the manual samples, which is evident in all of the marine deployments. It is likely that the SCAWS managed to capture chemical changes which were missed by conventional sampling. The most possible source for these changes should be the strong tidal phenomena in Southampton water. This is supported by previous studies (Hydes and Wright, 1999), where the tidal phenomena are linked to salinity and nutrient variations and from the salinity profile during the 2nd marine deployment (Figure 5-2, YSI-660 measurements).

Nitrate results cannot be assessed properly because of the significant errors that the analytical method entails (see section 4.5.2). However, in the last deployments nitrate profiles are more similar and concentrations are within the nitrate concentration region that other studies have identified. A more realistic assessment could be made if the sampler was deployed without the rhodamine injection system and nitrate determination of the SCAWS samples was performed with a conventional technique.

For trace metals the assessment is ambiguous. This is related to the fact that the deployments took place in an environment where concentrations of trace metals are variable. In addition to that, the fact that the samples have not been preserved properly during deployment possibly affected the

final result. Further deployment, laboratory tests and engineering modifications/additions of the sampler (e.g. sample preservation) should be considered for such sampling needs (see chapter 7).

Overall, the first marine deployments were an evolution test both for the sampler but also for the SCAWS project (evaluation tools, interpretation of results, etc.). During that period the sampler has improved, analytical methods have been customised to the project's needs and methods to optimise the preparation of the sampler for deployment and preparation of the samples for analysis were identified. Considering also the available time and the available resources for the project the first tests for the SCAWS were positive and encouraging

6 River Deployments

The MKII prototype was completed by January 2008. The MKII is autonomous and can be deployed, in shallow aquatic environments, for at least one month (duration of the power supply unit). The fact that the MKII prototype is autonomous, allows it to be deployed in a remote environment. As the sampler has not been tested in a fresh water environment, where chemistry and conditions are different from seawater, it was decided to deploy the sampler in a river in the New Forest (Lymington River). This site is close to Southampton and it was possible to visit it frequently, in order to monitor the sampler's performance and record ambient conditions (manual sampling, water flow, temperature, etc).

6.1 Environmental and Hydro geologic setting

The deployment site is in Lymington River in the New Forest (see Figure 6-1 and APPENDIX for geology map), where the Environment Agency (EA) maintains a flood warning station. The site has limited public access so the SCAWS is protected from New Forest "explorers". The station is located at a weir, where the EA has installed equipment to monitor and record the river runoff. Because of the weir, even in dry periods, the water level is sufficiently high so that the SCAWS's inlet is always under water. The flood warning station also allowed us to install a custom made platform, from which the SCAWS can be suspended (Figure 6-1).

The Lymington River follows a 30 km north to south route, through the New Forest, starting from Fritham, and ending in the Solent, at the town of Lymington (see Figure 6-1). The river is not influenced by tides because of tide gates that are installed near Lymington in order to prevent excessive flooding. The river has a catchment of 127 km^2, which runs over recent deposits of gravel and brickearth overlaying sands, silts and clays (see geological map in APPENDIX). The catchment is considered impermeable, which results in large river run offs during heavy rainfall. This is a general characteristic of the New Forest catchments; hence the EA has developed the New Forest Catchment Flood Management Plan (CFMP), part of which is the site where the SCAWS was deployed.

The area, like the rest of the New Forest, experiences periods with intensive tourist activity, but it is also valued for wildlife and forest conservation projects. Heavy industrial units are not present in the area and agricultural activity is evident but not intensive. New Forest ponies, horses, cattle and deer can be seen grazing along the river's banks (animal excretion can affect river water chemistry).

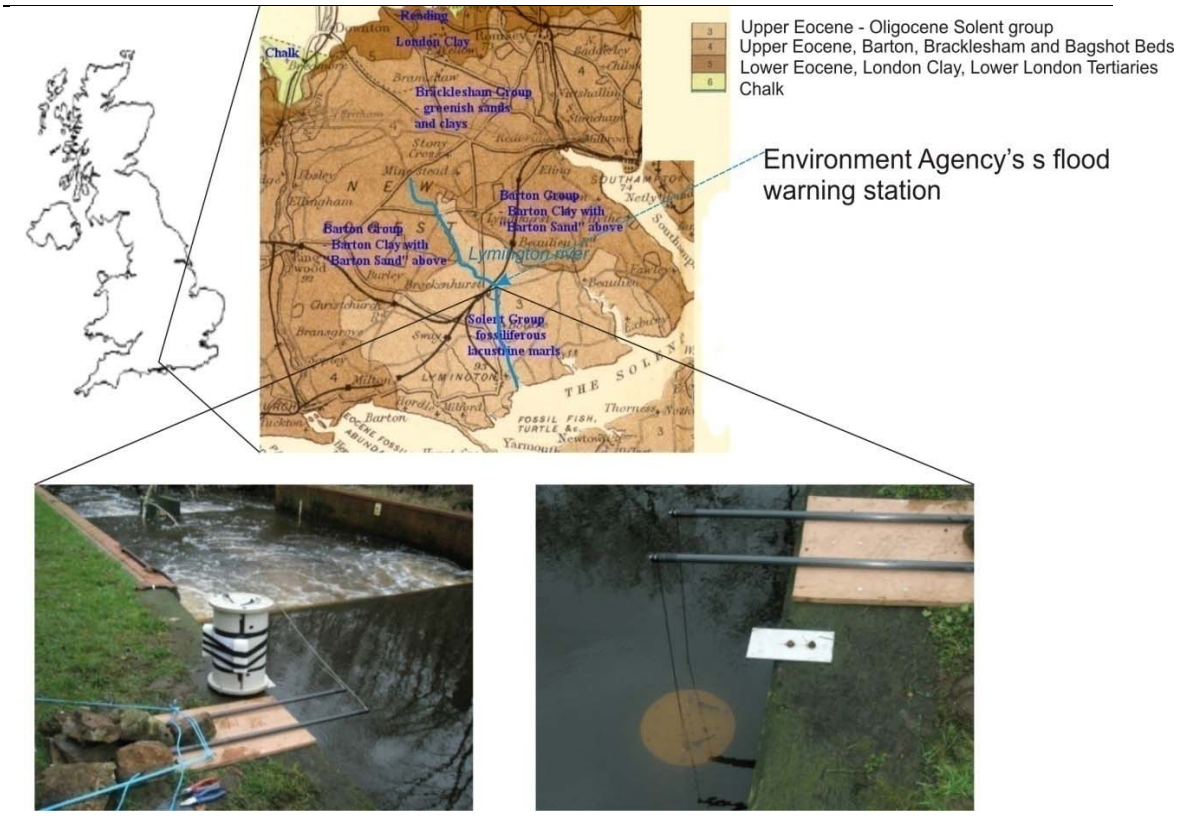


Figure 6-1: Deployment site in Lymington River, New Forest, Hampshire. The geological map is from Dr. Ian West's website (http://www.soton.ac.uk/~imw/Geology-Britain.htm). The bottom pictures show the deployment site and the custom made platform for the SCAWS.

6.2 Test Deployment

The first river deployment of the MKII prototype was for one week (25/01/2008 to 01/02/2008). The SCAWS was equipped with a 20m long sampling tube, and the tracer injection system was set to operate every day. The filter was set to be renewed every day, so that we gain a better picture of the new filter renewing mechanism (see section 3.2.4). Manual samples were collected every day (~12:00 pm). Water temperature and conductivity were also recorded, with a portable conductivity and temperature measuring system (conductivity meter: WTW LF320, sensor – conductivity cell: WTW TetraCon 325 (±0.1 µS/cm for conductivity, ±0.15 ^{o}C for temperature).

The first river deployment was to identify whether the specific sampling site is suitable for our research. The deployment period was short, so the interest of this deployment is not of particular hydrogeochemical importance. The results will be used only for the evaluation of the sampler.

6.2.1 Results

The ambient conditions during this deployment are presented in Figure 6-2.

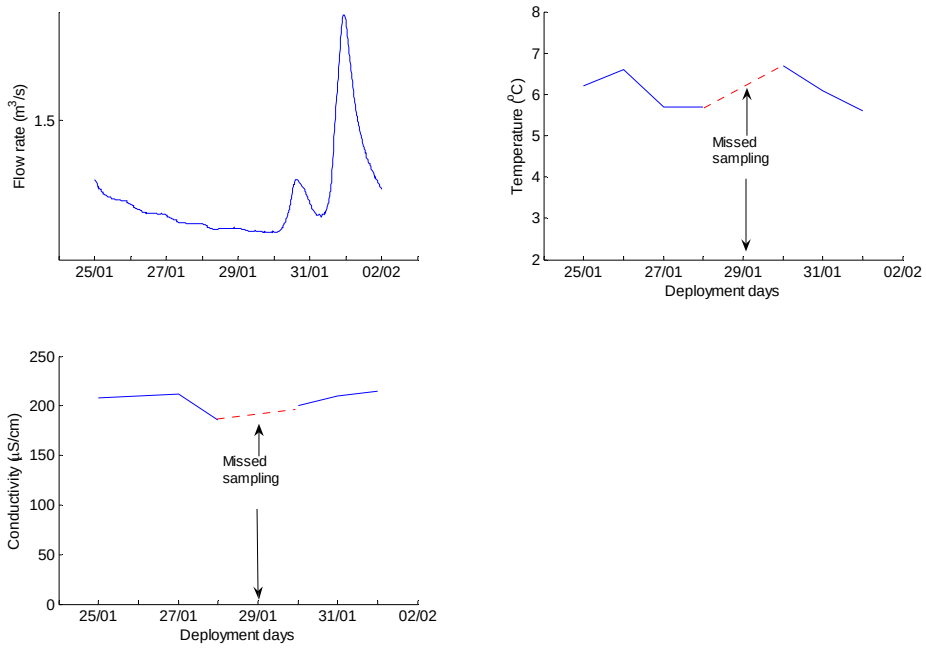


Figure 6-2: Ambient conditions during first river deployment (25/01/08 - 01/02/08). Flow rate data were obtained from the Environment Agency (15 min resolution records). Temperature and conductivity data are daily measurements, obtained when we visited the site.

From Figure 6-2, it is evident that river flow rate and conductivity variations were not large, which will probably be reflected in water chemistry as well. The increase in the river flow rate was caused by a short period of rainfall that lasted for a few hours. The temperature record suggests that the osmo pumps flow rate will be variable as well, but because the temperature is low, the magnitude of the flow rate variation will be smaller (lower end of the exponential line; see Figure 3-12).

After recovery of the sampler, it was evident that the tracer injection system did not operate properly. There were not as many rhodamine strips as expected (expected 8 strips and instead only the first 3 were visible). This happened because the batteries voltage was drained (the voltage of the batteries pack has dropped from 16V to 7.79V, within the one week period). This is more than likely related to low temperature, because during laboratory tests, such voltage drops, over that short period of time, were not evident. However, the encouraging fact was that the evident rhodamine strips matched the segmentation profile produced by the temperature – flow rate relationship. The segmentation of the tube is presented in Table 6-1.

Date	Temperature (°C)	Flow rate (ml/d)	Theoretical length (cm)	Rhodamine length (cm)
26/01/2008	6.6	1.12	142	145
27/01/2008	5.7	1.08	137	140
28/01/2008	5.7	1.08	137	140
29/01/2008				*140*
30/05/2007	6.7	1.12	143	142
31/01/2008	6.1	1.09	139	136
01/02/2008	5.6	1.07	137	141

Table 6-1: Theoretical and rhodamine segmentation profiles for the 1st river deployment. The red italic value was produced arbitrarily, as the site was not visited at that day. Temperature was not recorded and the rhodamine strip was missing.

The battery voltage drain also affected the filtering system. This was evident from the fact that the spool which collected the used filter did not have the expected amount of mesh. When the batteries were recharged, in the laboratory, the system operated properly.

6.2.1.1 Comparison between SCAWS and manual samples

The concentration profiles of major anions and cations, for both the manual samples (for collections and treatment procedures see section 4.3.2.1) and the SCAWS samples are presented in Figure 6-3.

Results for the major anions and cations are from the DX500 system.

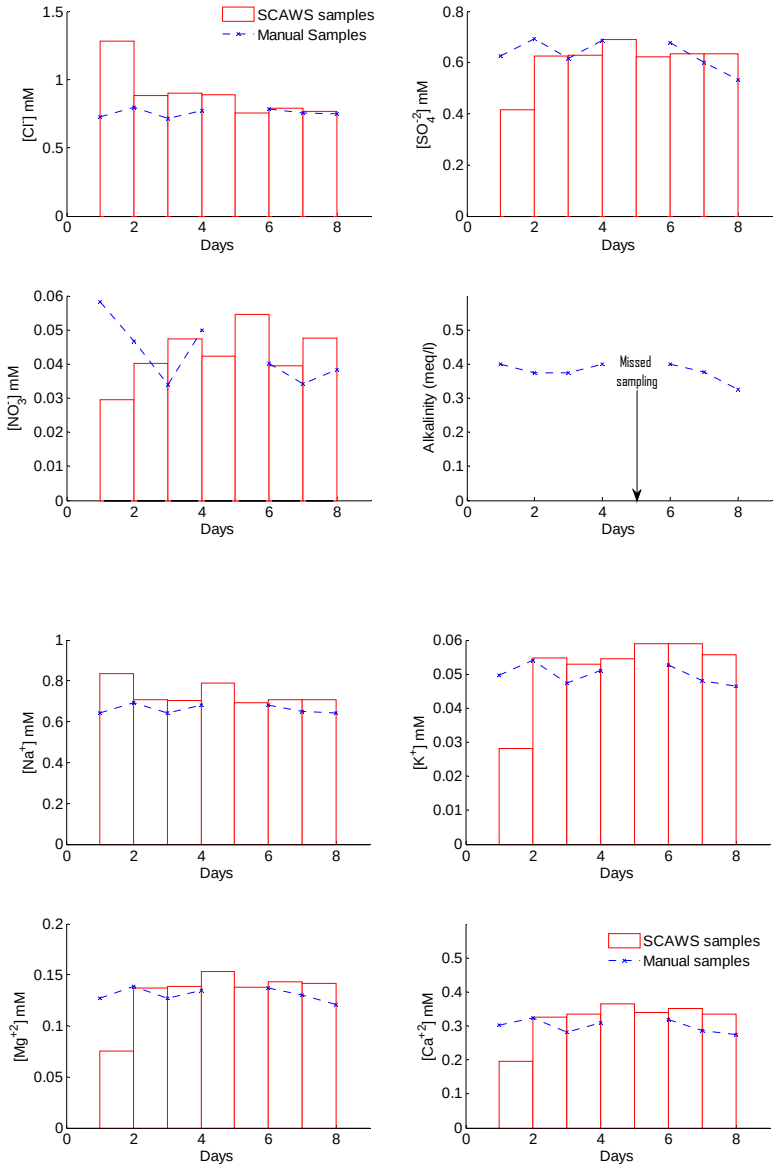


Figure 6-3: Comparison of major anions and cations between SCAWS and manual samples for the test river deployment. Results are from analysis with the IC DX500 system.

6.2.1.2 River water geochemistry

The data can be used to identify basic geochemical indices, which will provide a more detailed picture of the river water. A useful parameter is the ionic balance of the waters. Natural waters are thermodynamically stable – neutral. Acceptable differences between the total measured anions and total measured cations are generally considered to be ±5% (Johnson *et al.*, 1979). Larger variations may be associated to a systematic error of the analytical method, or to different ionic species (e.g polar humic substances), which contribute to the ionic charge, but were not determined. The charge

balance can be used to obtain a first estimate of the organic anions concentration and of the dissolved organic carbon (DOC) reactivity (Christophersen *et al.*, 1994). Berner (1996) suggests that:

$$T_z^+ = T_z^- + T_{org} \qquad \textbf{6-1}$$

Where T_z^+ is the total inorganic cationic charge, T_z^- is the total inorganic anionic charge and T_{org} is the total charge from organic ions.

The anionic and cationic charge of the waters contributed by the major ions is calculated from equations 6-2and 6-3. Results are presented in Figure 6-4.

$$T_z^+ = Na^+ + K^+ + 2 \cdot (Ca^{+2} + Mg^{+2}) \text{ in meq/l} \qquad \textbf{6-2}$$

$$T_z^- = Cl^- + NO_3^- + 2 \cdot SO_4^{-2} + HCO_3^- \text{ in meq/l} \qquad \textbf{6-3}$$

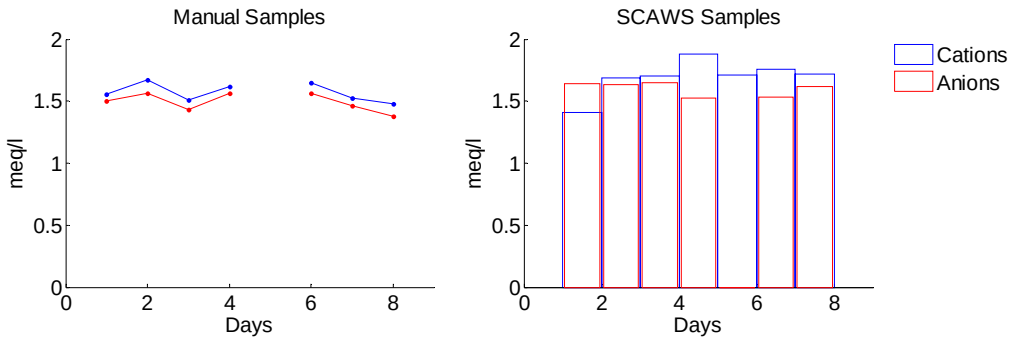


Figure 6-4: Ionic balance of manual and SCAWS samples for the test river deployment.

The major objective of this initial deployment was to test the performance of the sampler. Hence the geochemical significance of these data will not be evaluated further at this stage. Discussion is presented in section 6.2.2.

6.2.2 Discussion of river test deployment

6.2.2.1 Mechanical performance

The mechanical performance of the sampler during this deployment was not very stable and was considered controversial. In general terms it was positive that the sampler operated continuously and the pump "survived" in a potentially harsh environment.

However, the mechanical operation of the sampler's innovative parts was problematic. The problem was identified (batteries) and the solution for it, was to install a more robust and efficient battery pack. For this we have decided to equip the sampler with an industrial type 15V battery with 7000 mAh amperage. The system has not yet been fully tested (future plans see chapter 7).

The fact that the three rhodamine strips matched the temperature – flow rate profile, was encouraging. Also the fact that the renewing mechanism operated for the first three days was also positive. As expected the fact that the nylon mesh was not renewed did not affect sampling, because during this short period of time, the mesh did not clog.

6.2.2.2 Chemical performance

The overall "chemical" performance of the sampler can also be considered positive. The concentration profiles of SCAWS samples and manual samples are similar and within the analytical uncertainties (see section 4.3.1), both for major anions and cations. The first samples collected from the SCAWS, have higher concentration of chloride and sodium than manual samples, which is related to contamination from the rhodamine (see section 3.2.3). This is supported by the fact that after the third day and the "malfunction" of the tracer addition system, the SCAWS samples have the same chloride and sodium profiles as the manual samples. The small differences, between the two sampling methods, may be related to analytical uncertainties, but it is more possible that these differences are related to the fact that the SCAWS integrates changes that are happening during the sampling interval, while manual samples only provide a "chemical" snapshot of the environment.

Because of the small number of samples (7), and because the concentration range of solutes is rather limited, a correlation between the data resulted from the manual samples and the SCAWS samples will not provide coherent and robust information of the sampler's reliability. This will be addressed during the section discussing the one month deployment (see section 6.3.2.1).

The ionic balance profiles for both sampling methods during the deployment period (Figure 6-4) show that there is a deficit of anions, indicating the presence of humic ionic substances that were not determined in this study.

6.3 Mid-term Deployment

The results from the one week river deployment were encouraging; therefore, it was decided to redeploy the sampler at the same site for a longer period. Unfortunately the electronic circuit (data logger) failed during laboratory tests a few days before the planned deployment date. The repair time was estimated to be long (3 to 5 weeks), so alternative options had to be considered. It was decided to deploy the sampler only with the tracer injection device and activate it manually every day. To do this the solenoid pump's electrical connection cable was connected to a switch (ON/OFF) and a 16V battery pack. The filtering device was not installed as it requires the data logger to operate.

This deployment does not provide a complete picture of the SCAWS's performance as one of the two innovative parts is not tested in real conditions. However, even in the absence of the filtering mechanism we will still be able to:

- Evaluate the performance of the time stamping system over a period of one month, during a deployment in a natural environment.
- Collect manual samples at the same period and give the opportunity to make a coherent and realistic comparison of the "SCAWS" samples with the "Manual" samples..

The sampler was deployed for a period of one month (13/05/08 – 12/06/08). Ambient conditions and results from this deployment are presented in sections 6.3.1and 0 respectively.

6.3.1 Conditions

For a 30 days sampling period and assuming the river water temperature is 15 ^{o}C, the sampling tube should be 60 m long (see section 3.2.2). Hence the sampler was equipped with a 80 m sampling tube, which was adequate for the one month deployment.

Ambient conditions, during this deployment were recorded with the same means as in the previous river (test) deployment. The ambient data are presented in Figure 6-5.

As is evident from Figure 6-5, environmental conditions during the deployment period were variable. On the 13th day of the deployment, and after a dry period of approximately 4 weeks the flow of the river increased significantly (from 0.5 m^3/s to 25 m^3/s) due to heavy rain. This resulted in a drop in conductivity and a significant increase in suspended solids.

A second rain event occurred a few days later, where conductivity dropped and suspended solids increased. It is evident that the conductivity (dissolved ions), dropped to the same value as the previous event, but the suspended solid increase was an order of magnitude smaller than the previous increase. This observation suggests that the first rain event removed the loose sediment that had accumulated during the dry period. The lower increase of suspended matter during the second rain event suggests that there had not been enough time for the reservoir of loose sediment to build up after first rain event. The conductivity profile indicates that the conductivity had dropped to a similar level during the second rain event.

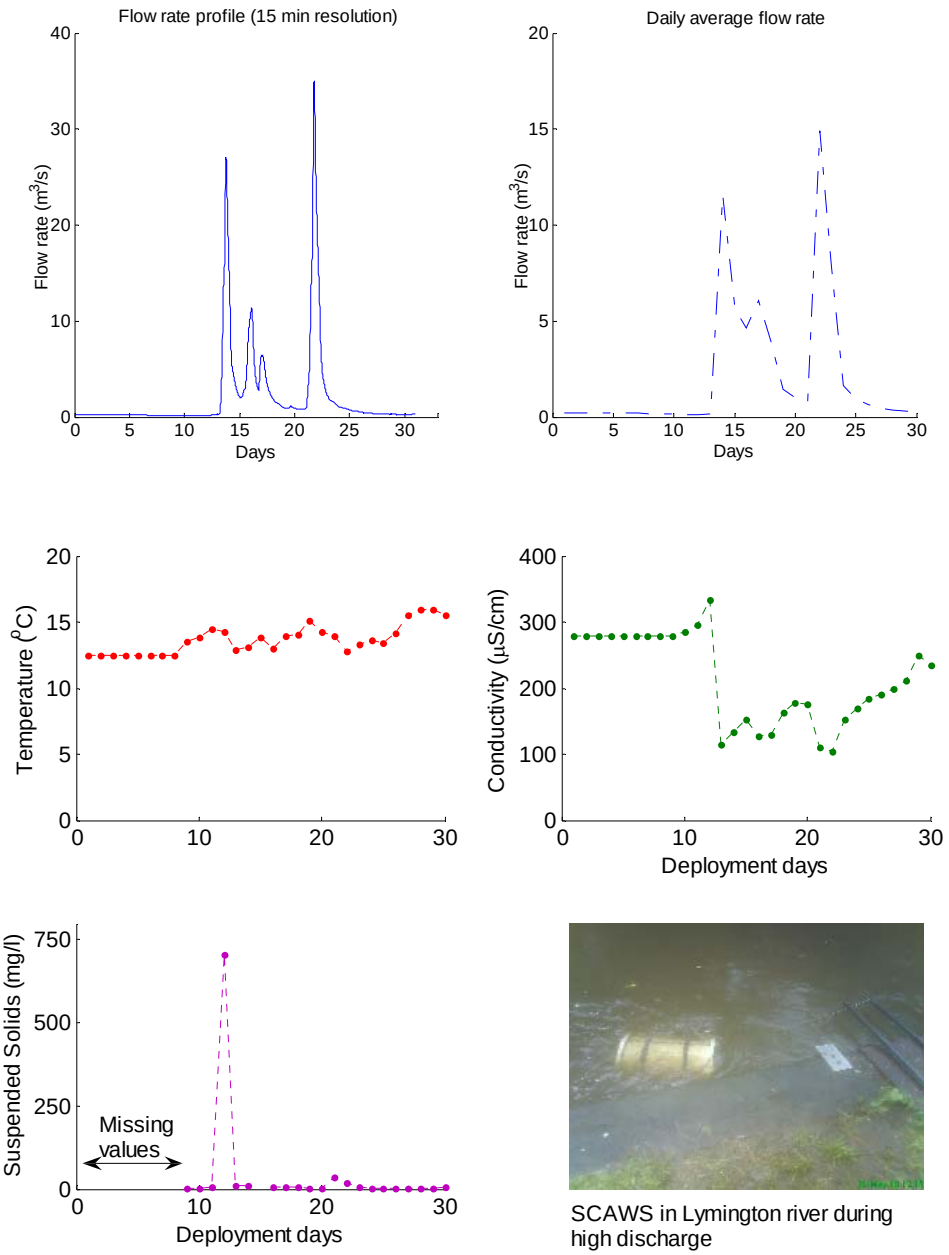


Figure 6-5: River Water conditions, during 30 day deployment (14/05/08 – 12/06/08). All parameters indicate the variability of ambient conditions during the deployment period. The 15 minute resolution flow rate profile is produced from data provided by the Environment Agency, taken from the gauge station in Lymington River.

6.3.2 Results

The processing of the samples was similar to the previous deployments. As with the previous deployments, the segmentation profile from the rhodamine strips matched the theoretical profile. Results are presented in Table 6-2.

Days	Temperature (°C)	Theoretical flow rate (ml/d)	Theoretical length (cm)	Real length (cm)
1	12.5	1.23	180	179
2	12.5	1.23	180	179
3	12.5	1.23	183	177
4	13.0	1.27	187	180
5	13.5	1.31	187	185
6	13.5	1.31	187	187
7	13.5	1.31	187	187
8	13.5	1.31	187	188
9	13.5	1.31	189	187
10	13.8	1.33	195	189
11	14.5	1.39	193	195
12	14.3	1.37	183	195
13	12.9	1.26	184	181
14	13.1	1.28	189	183
15	13.8	1.33	183	190
16	13.0	1.27	191	184
17	14.0	1.35	191	193
18	14.1	1.36	199	192
19	15.1	1.44	193	202
20	14.3	1.37	191	194
21	14.0	1.35	182	192
22	12.8	1.26	185	181
23	13.3	1.29	188	186
24	13.6	1.32	186	188
25	13.4	1.30	192	186
26	14.2	1.36	202	191
27	15.5	1.47	206	202
28	16.0	1.51	206	210
29	15.9	1.51	202	211
30	15.5	1.47	194	210

Table 6-2: Segmentation profile and sample production of the one month river deployment. The theoretical flow rate was calculated using the parameters from the July 2008 experiments (see section 3.3.1).

6.3.2.1 Comparison between SCAWS and Manual Samples

Concentration profiles of major ions for the manual samples and the samples from osmo samples are presented in Figure 6-6 (original data are presented in the APPENDIX).

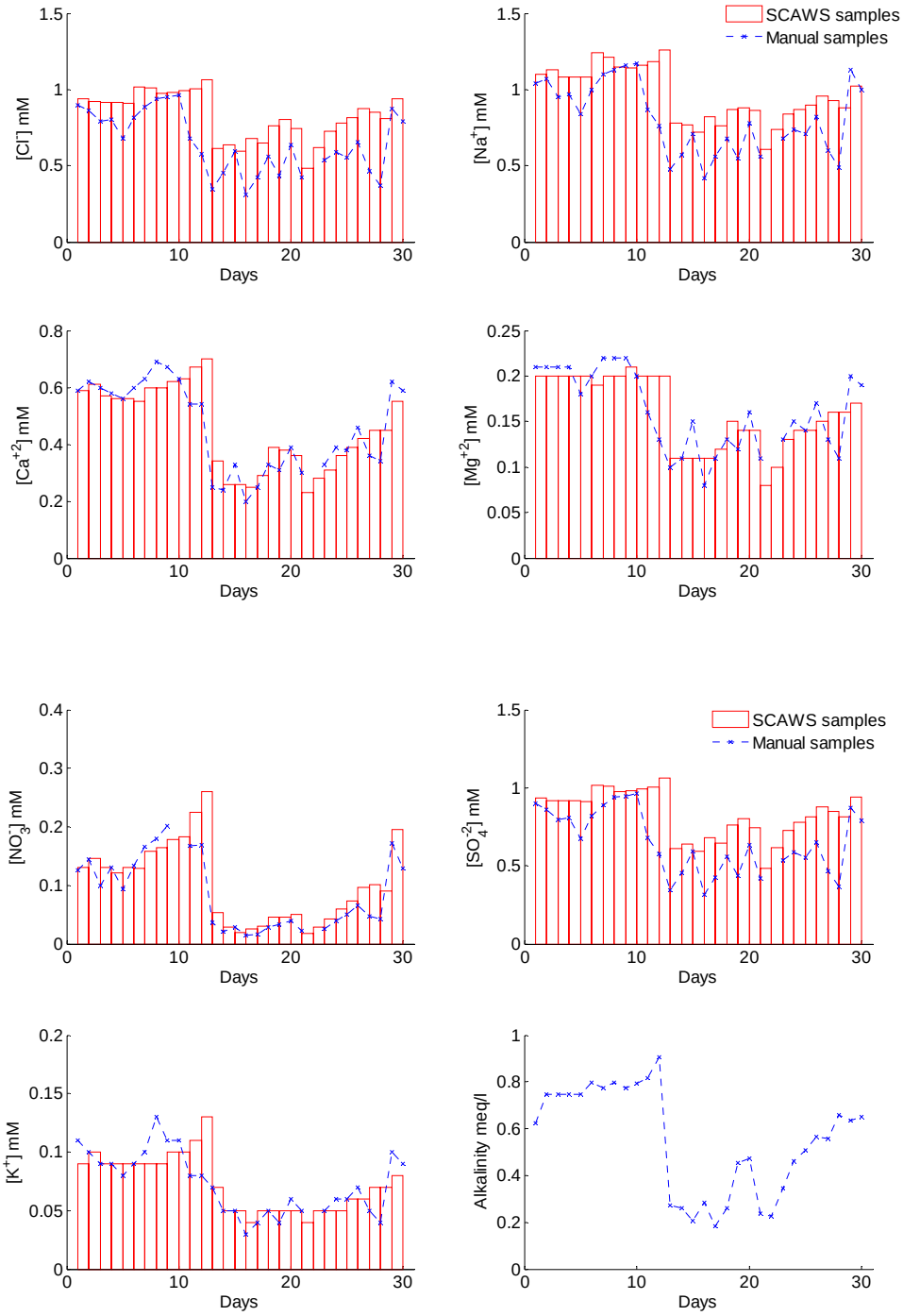


Figure 6-6: Comparison between manual and SCAWS samples, for the one month river deployment. Results are from the DX500 system. Phosphate concentrations in all samples were below the detection limit of the IC25 chromatography system (0.1 µM).

By way of comparison, 1:1 correlations of the two sampling methods are presented in Figure 6-7 and the correlation parameters are presented in Table 6-3.

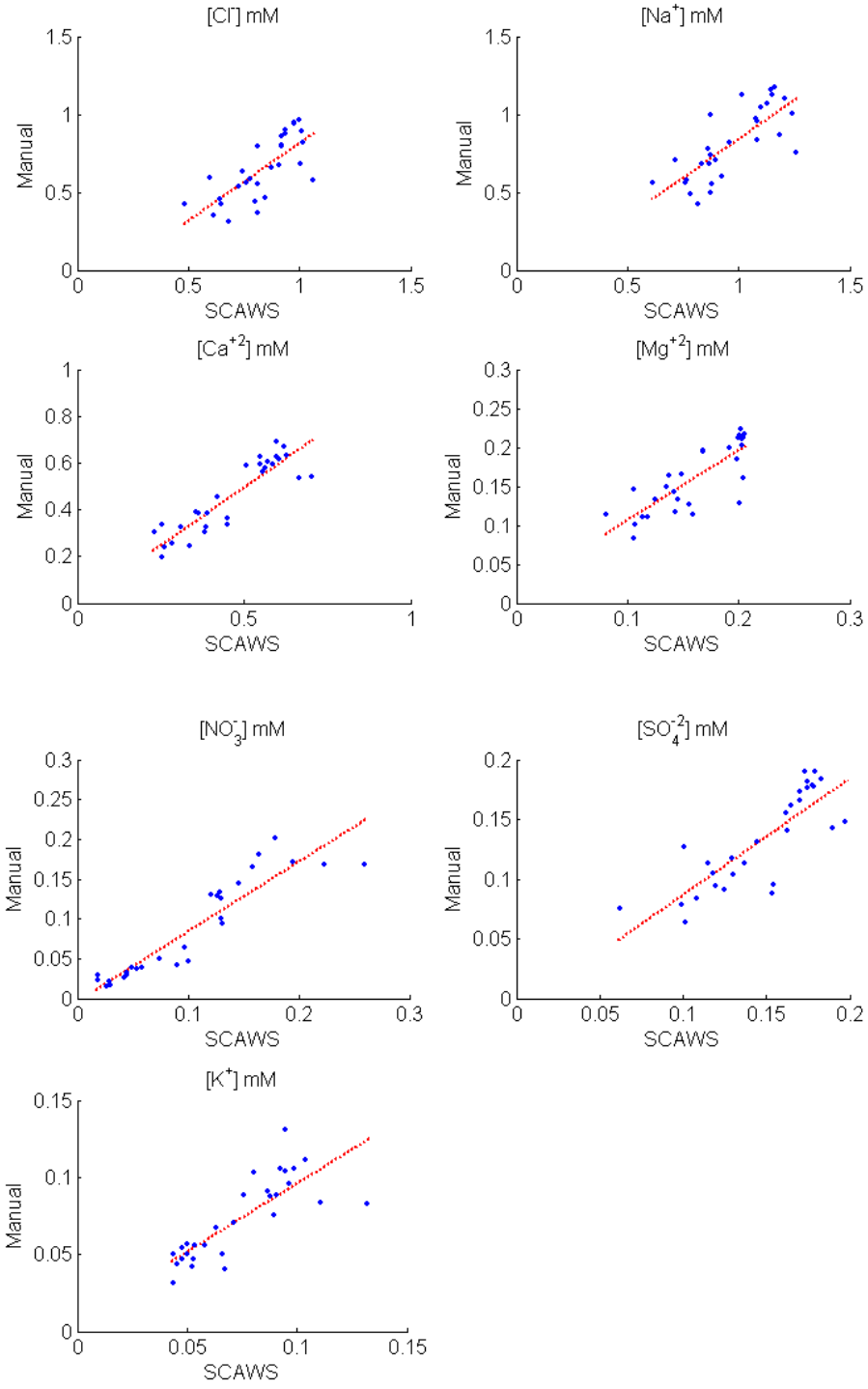


Figure 6-7: Correlation of the two sampling methods for major anions and cations.

	Manual vs. SCAWS		SCAWS vs. Manual	
Solute	a	R^2	a	R^2
Na^+	0.841±0.059	0.559	1.151±0.081	-0.049
Cl^-	0.795±0.063	0.518	1.22±0.085	-0.368
Ca^{+2}	0.988±0.053	0.805	0.993±0.053	0.77
Mg^{+2}	0.995±0.059	0.648	0.982±0.048	0.578
NO_3^-	0.851±0.075	0.855	1.118±0.082	0.829
SO_4^{-2}	0.905±0.058	0.672	1.075±0.069	0.451
K^+	0.976±0.078	0.633	0.982±0.065	0.549

Table 6-3: Regression parameters between the two sampling methods. Regression follows a y=a·x model.

The regression model that we used is the y=a·x. The ideal correlation, which will indicate that there are no difference between the two sampling methods is a=1 and R^2=1(Miller and Miller, 1988).

The chloride and sodium profiles, show significant differences, which are attributed to the rhodamine contamination (see section 3.2.3). The comparison between the two sampling methods of the corrected parameters is presented in Figure 6-8 and regression parameters (y=a·x) are presented in Table 6-4.

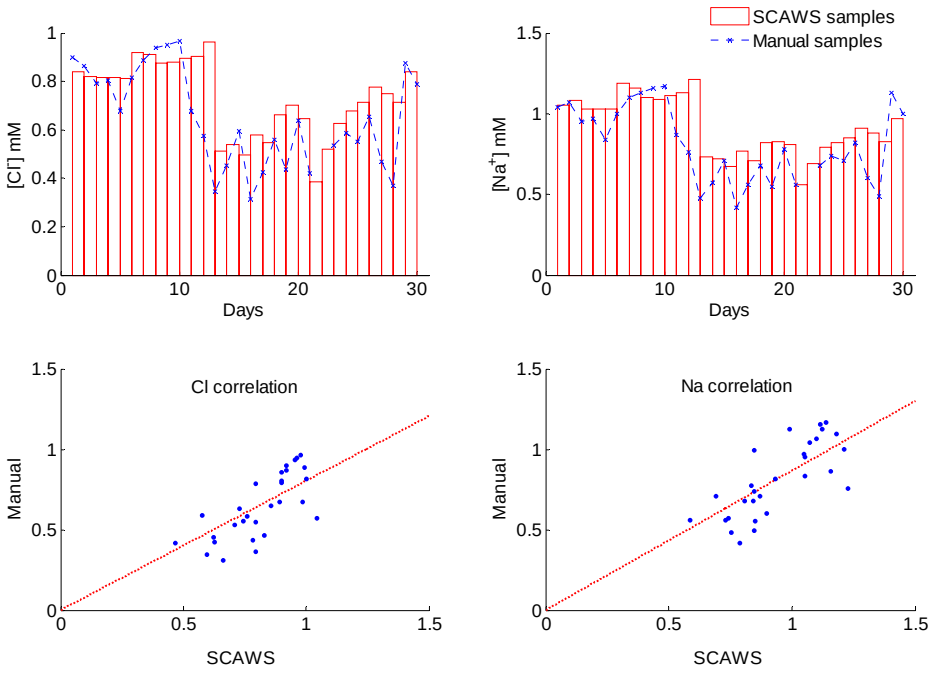


Figure 6-8: Rhodamine correction for chloride and sodium. Regression is of the y=a·x type. Parameters are presented in. Table 6-4.

	SCAWS vs. Manual		Manual vs. SCAWS	
Solute	a	R^2	a	R^2
Na^+	0.8854±0.062	0.57	1.094±0.022	0.068
Cl^-	0.8892±0.069	0.536	1.081±0.085	-0.028

Table 6-4: Correlation of sodium and chloride after rhodamine correction. Correlations are not significantly improved.

All the calculations concerning sodium and chloride that will be presented in the next sections have been performed using the rhodamine corrected concentrations (0.1 mM for Cl^-, 0.05 mM for Na^+).

The concentration profiles, for some trace metals are presented in Figure 6-9. As can be seen differences between the sampling methods are large. One reason for this may be the absence of a preservative (acid: HCl or HNO_3), without which trace metals are more than likely to attach to the sampling tube's walls, which results to loss of dissolved trace metal concentration. This can be supported by the fact that trends of trace metal concentration profiles are similar, which might suggest that the difference between the two profiles has been lost on the sampling tube walls. The geochemical significance of the trace metal data will be discussed in section 6.3.3.3.

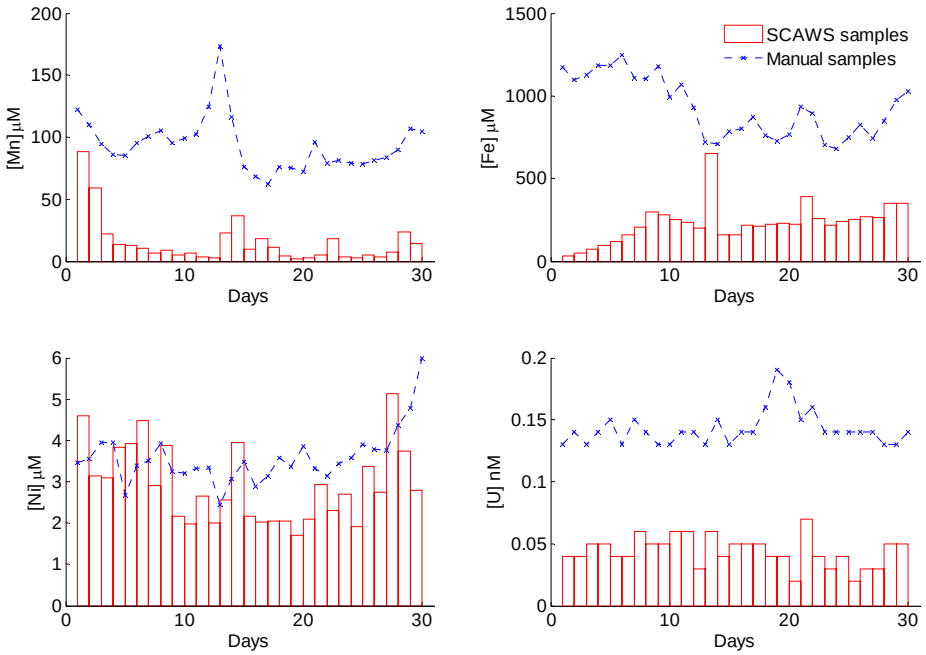


Figure 6-9: Comparison of trace metal concentration profiles between SCAWS samples and manual samples (14/05/08 - 12/06/08). The concentration profiles indicate the significant difference between the two sampling methods.

6.3.3 Discussion of the one month deployment results

6.3.3.1 Mechanical performance

Concerning the mechanical performance of the sampler during this deployment period, the main outcome was that sampling was continuous and undisturbed during the deployment period. More importantly during this period environmental conditions were, sometimes, very hostile for any equipment that was installed in the river (see image in Figure 6-2), but the design proved reliable and robust.

During the deployment period, activation of the micro-solenoid pump was also consistent and stable. The fact also that the rhodamine segmentation profile was accurate, over a one month period was very encouraging.

As has been mentioned the SCAWS was deployed without the filtering device. Even without it sampling was not compromised. Also there was no evidence of biofouling or aggregate matter inside the sampling tube. As was presented in Figure 6-6, this did not affect analysis of major anions and cations, but – as expected – the absence of a filtration and/or preservation (acid addition) system is the main reason for the differences of trace metal concentrations, between the SCAWS samples and manual samples.

6.3.3.2 SCAWS sampling and "chemical" performance

This deployment was the first, during which environmental conditions changed significantly within a very short period of time and had a direct effect on water chemistry. The fact that the concentration profiles match exactly with environmental conditions (dilution of concentration because of heavy rain – see Figure 6-10) demonstrate that the SCAWS performed well and the collected time series samples present changes in water chemistry.

The performance of the sampler can be evaluated from Figure 6-6 and Figure 6-7.

Concentration profiles between the two sampling methods have similar trends. 1:1 correlations between the manual and SCAWS samples (see Figure 6-7) have correlation coefficients (R^2) ranging from 0.52 to 0.85 (see Table 6-3). The slope of the correlation lines range from 0.78 to 0.998. Differences from the ideal correlation ($a=R^2=1$) can be related to the inherent difference of the sampling methods. Osmo samplers integrate differences that occur during the sampling resolution interval (for the SCAWS case this is 1 day), when manual samples provide a chemical "snapshot" of the aquatic environment. In addition, errors associated with the analytical methods (see chapter 4), will contribute to any deviations from the ideal correlations.

For chloride and sodium even after the rhodamine correction, correlations do not improve. This suggests that differences between the two sampling methods can reflect actual concentration differences, which can be attributed to the reasons mentioned in the previous paragraph. Especially

for sodium and chloride, during increased rainfall short term changes (diurnal or even hourly) in their concentrations can be significant (cyclic salt contribution see section 6.3.3.3 for further discussion).This indicates the need for a finer temporal resolution (e.g. every 12 hours) of the SCAWS samples, when there is evidence of short term changes of significant magnitude. This is further discussed in section 7.2.2.

Nitrate present the best correlation profile ($R^2 = 0.86$). This is very encouraging, because nitrate concentrations were expected to be altered (lack of oxygen or reducing bacteria can reduce nitrate to nitrites, nitrogen, etc.) as no preservative was added to the SCAWS samples during collection. However this did not occur, indicating that even for sensitive solutes the SCAWS is reliable. Deployment of the sampler over longer periods will provide a more coherent picture of the sampler's ability to retain integrity of nitrate.

The dilution of the river water from the excessive rain was captured by the SCAWS and the signal has been preserved in the sampling tube during the deployment period. Moreover, the fact that between the two daily samples (before and after dilution) the concentration difference is large and immediate, indicates that dispersion and diffusion of dissolved/soluble ions in the sampling tube are minimized. In addition to this fact, concentration profiles demonstrate the good response of the sampler to rapid and high magnitude changes. From Figure 6-5 (River discharge record with a 15 min sampling resolution), it is obvious that the event was very rapid and the dilution was very fast. From the EA's discharge record it is found that the maximum flow rate was developed in less than 13 hours (from 0.7 m^3/s to 27 m^3/s).

6.3.3.3 Geochemistry

The data that were collected can be used to identify basic geochemical indeces. As with the previous (test) deployment, ionic balances may give an insight into the dissolved organic matter that has not been determined analytically.

The ionic balance profiles during the deployment period, for both sampling methods are presented in Figure 6-10. The ionic balance was calculated from equations 6-3 and 6-5. One point that should be noted is that for the anionic balance calculations of the SCAWS samples, alkalinity values are taken from the manual samples.

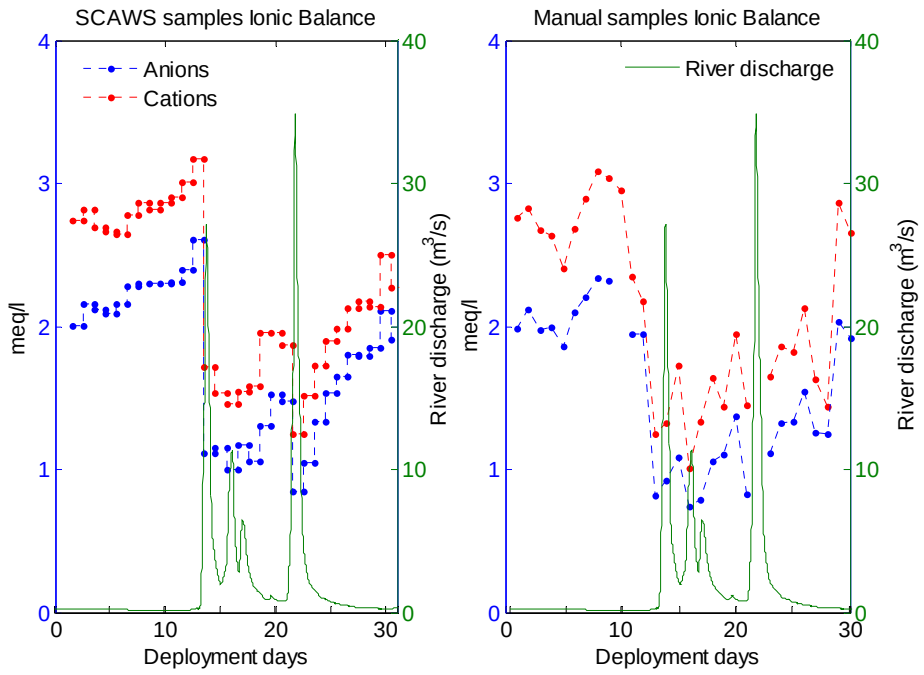


Figure 6-10: Ionic balance for SCAWS and manual samples during the one month river deployment. In the SCAWS ionic balance the chloride and sodium concentrations are corrected for the rhodamine contamination (0.1 and 0.05 mM respectively). For both sampling methods the alkalinity values are the same and taken from the manual samples.

Correlation between the cationic and anionic charge for both sampling methods is presented in Figure 6-11. The total cationic charge varies from 0.8 meq/l (low), to 3 meq/l (high).

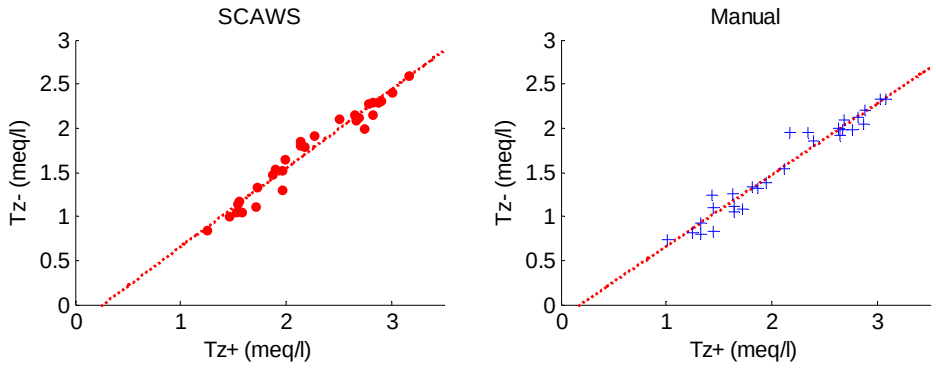


Figure 6-11: Ionic balance correlation between the two sampling methods. Correlation coefficients (R^2) for a linear model (y=a·x+b) are 0.963 and 0.948 for SCAWS and manual samples respectively. Interception of the x-axis indicates the presence of organic acids.

	a	b	R^2
SCAWS	0.89 ± 0.033	-0.30±0.076	0.963
Manual	0.81 ± 0.036	-0.15±0.079	0.949

Table 6-5: Regression parameters for cationic and anionic charges.

From the ionic balance it is evident that during the deployment period cationic charge was higher than the anionic. The difference should be attributed to the dissolved organic matter of the river.

Correlations between cationic and anionic charge from the two sampling methods are similar (see Table 6-5). The ionic balances present a deficit of anions, which can be related to the presence of organic acids derived from degrading vegetation (Berner and Berner, 1996; Edmond *et al.*, 1996). This is further supported by the high iron concentration of the river (see Figure 6-9, Fe~ 20 μM) (Berner and Berner, 1996; Jarvie *et al.*, 2008).

The major ions data can be compared against data from the UK Environment Agency database of various sampling sites along the Lymington River (some of the sites are presented in Figure 6-12).

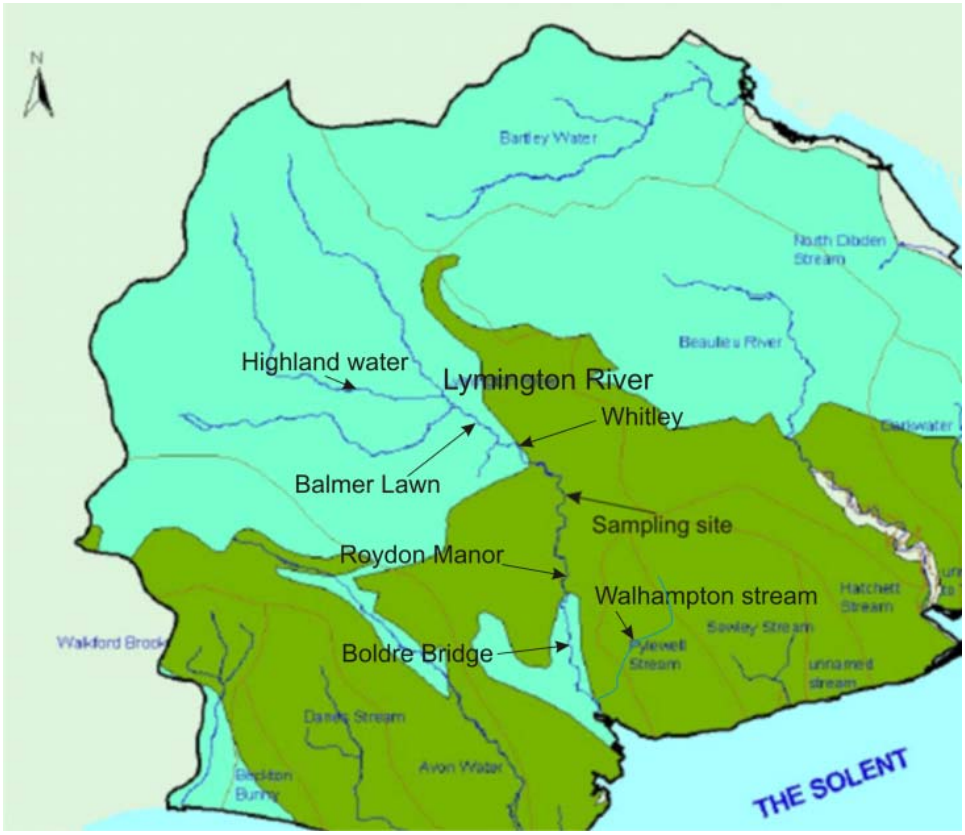


Figure 6-12: UK Environment Agency sampling sites along the Lymington River

The EA data cover mainly temporal and spatial variations of nitrate and chloride concentrations. Some of the data are illustrated in Figure 6-13.

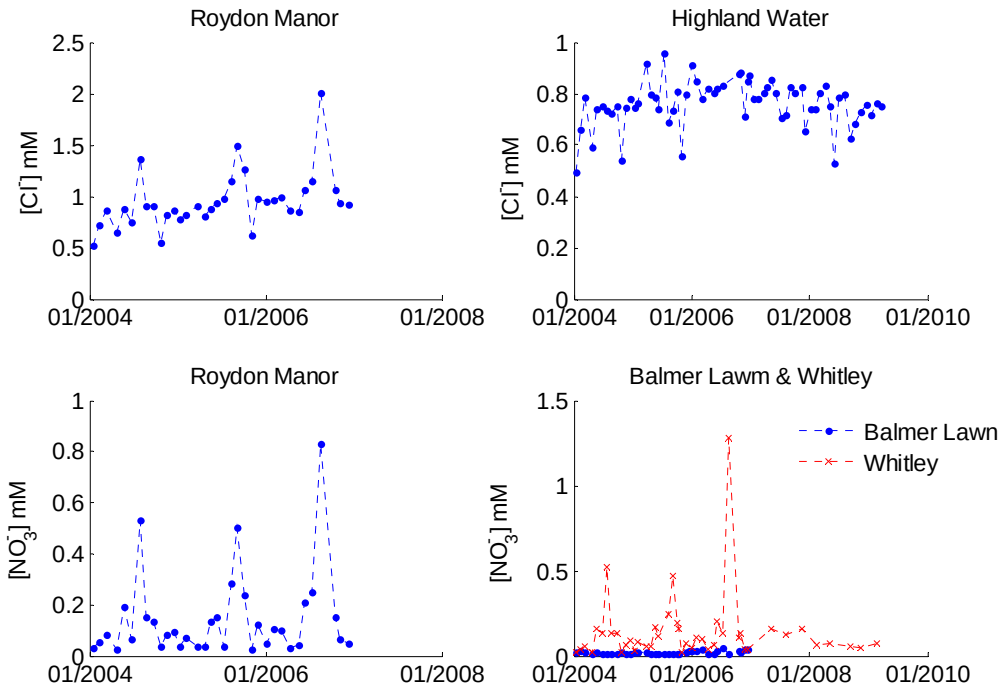


Figure 6-13: Chloride and nitrate temporal variations along the Lymington River.

The most interesting feature of these data is the big differences in nitrate concentrations along the Lymington river. A possible source of nitrates can be a municipal wastewater treatment plant that is operating in the Balmer Lawn area. The wastewater treatment plant operates after the Balmer Lawn sampling point but any discharges were captured further down the river. What is evident also is that the high nitrate peaks end in 2007, and since then the nitrate concentrations are more stable.

Comparing the data gained from the SCAWS and manually during the SCAWS deployment period against the above data, it is encouraging to find that chloride and nitrate concentrations are within the same order of magnitude.

In Figure 6-14 chloride and nitrate time series data from this study are plotted together with chloride – nitrate time series data from the Roydon Manor sampling station (see Figure 6-12 for sampling site location). All data sets present a linear relationship between the two parameters

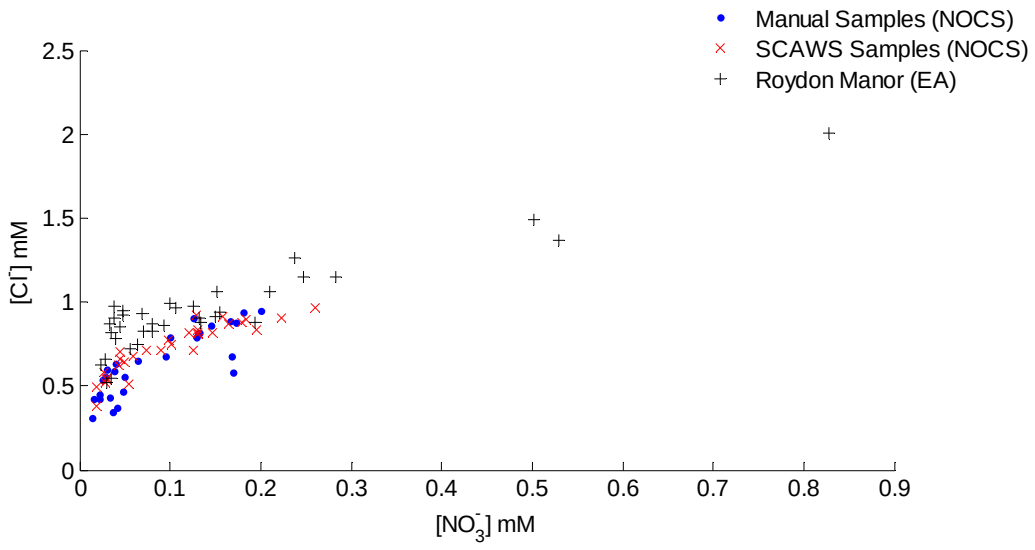


Figure 6-14: Chloride and nitrate comparison of SCAWS project and EA data. Regression parameters (least squares; y=ax+b model) are presented in Table 6-6.

	Manual	SCAWS	EA/Roydon Manor
a	2.66	2.01	1.49
b	0.41	0.52	0.73
R^2	0.72	0.81	0.84

Table 6-6: Regression parameters for chloride - nitrate relationship in Lymington river. Linear regression (y=ax+b) model.

For the rest of the major ions data are very sporadic; e.g. calcium and magnesium values along the Lymington river are available only for two dates (14/01/2004 and 07/01/2004). Comparison between the EA data for Ca and Mg and the data from the SCAWS project is not feasible as the two sets are very different. As an indication it is reported the average Ca along the river on 14/01/04 is 0.18 mM – max 0.26, min 0.11 mM; and for Mg average is 0.084 mM – max 0.098 , min 0.064 mM. These concentrations can be found also in this projects data set.

Further analysis of the data will follow some basic analysis patterns that are found in literature (Stallard and Edmond, 1981, 1983, 1987; Edmond *et al.*, 1995; Berner and Berner, 1996) . The results however will be interpreted for the Lymington river's catchment size and geology, so insights of similar size catchments should be considered (Bricker *et al.*, 1994; Johnson *et al.*, 1994; Neal, 1999; Jarvie *et al.*, 2000a; Jarvie *et al.*, 2000b; Jarvie *et al.*, 2008).

Relationships between sodium and chloride, calcium and sulphate and calcium and magnesium with alkalinity can indicate the weathering (hence presence) of evaporites and carbonates. Dissolution reactions are presented in Table 6-7. Property – property diagrams of the relationships presented in Figure 6-15.

Reaction	Molar Ratio of products in solution
$NaCl \rightarrow Na^{+}+Cl^{-}$	$Na^{+}/Cl^{-}= 1:1$
$CaSO_4 \cdot 2H_2O \rightarrow Ca^{+2} + SO_4^{-2} + 2H_2O$	$Ca^{+2}/(0.5HCO_3^{-}+SO_4^{-2}) = 1:1$
$CaCO_3+H_2CO_3 \rightarrow Ca^{+2}+2HCO_3^{-}$	$Ca^{+2}/(0.5HCO_3^{-}) = 1:1$
$2CaCO_3+H_2SO_4 \rightarrow 2Ca^{+2}+SO_4^{-2}+2HCO_3^{-}$	$Ca^{+2}/(0.5HCO_3^{-}+SO_4^{-2}) = 1:1$
$2CaMg(CO_3)_2+2H_2CO_3 \rightarrow 2Ca^{+2}+Mg^{+2}+4HCO_3^{-}$	$(Ca^{+2}+Mg^{+2})/(0.5HCO_3^{-}+SO_4^{-2}) = 1:1$
$2CaMg(CO_3)_2+2H_2SO_4 \rightarrow$ $2Ca^{+2}+2Mg^{+2}+2SO4^{-2} + 4HCO_3^{-}$	$(Ca^{+2}+Mg^{+2})/(0.5HCO_3^{-}+SO_4^{-2}) = 1:1$

Table 6-7: Weathering reactions for evaporites and carbonates (Berner and Berner, 1996).

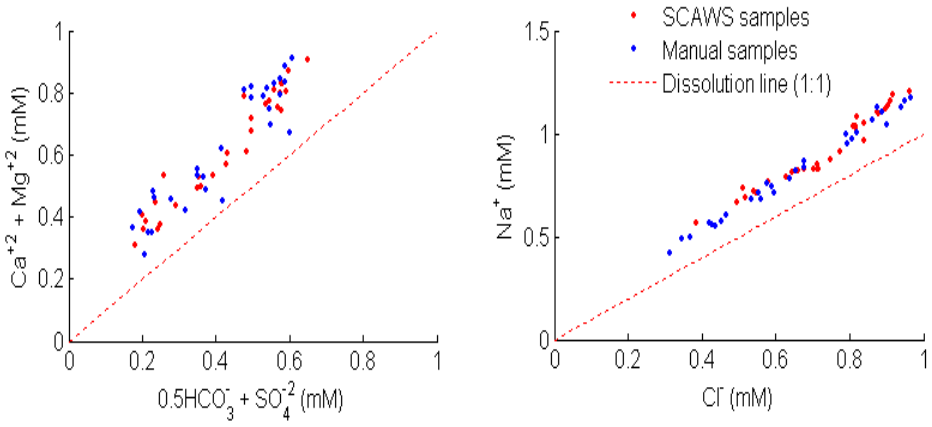


Figure 6-15: Property-property diagrams indicating whether there is weathering of evaporites and carbonates. Red lines represent the dissolution line.

According to Stallard and Edmond (1983) part of the weathering-geochemical picture of a catchment can be obtained from the relationship of the solutes with the total cations. More specifically, if the river drains evaporites, the ratio of sodium and chloride to total cations should increase with concentration. In the same study they suggest that rivers draining marine sediments and red beds, potassium has a low correlation with total cations at high levels (>0.2 meq/l).

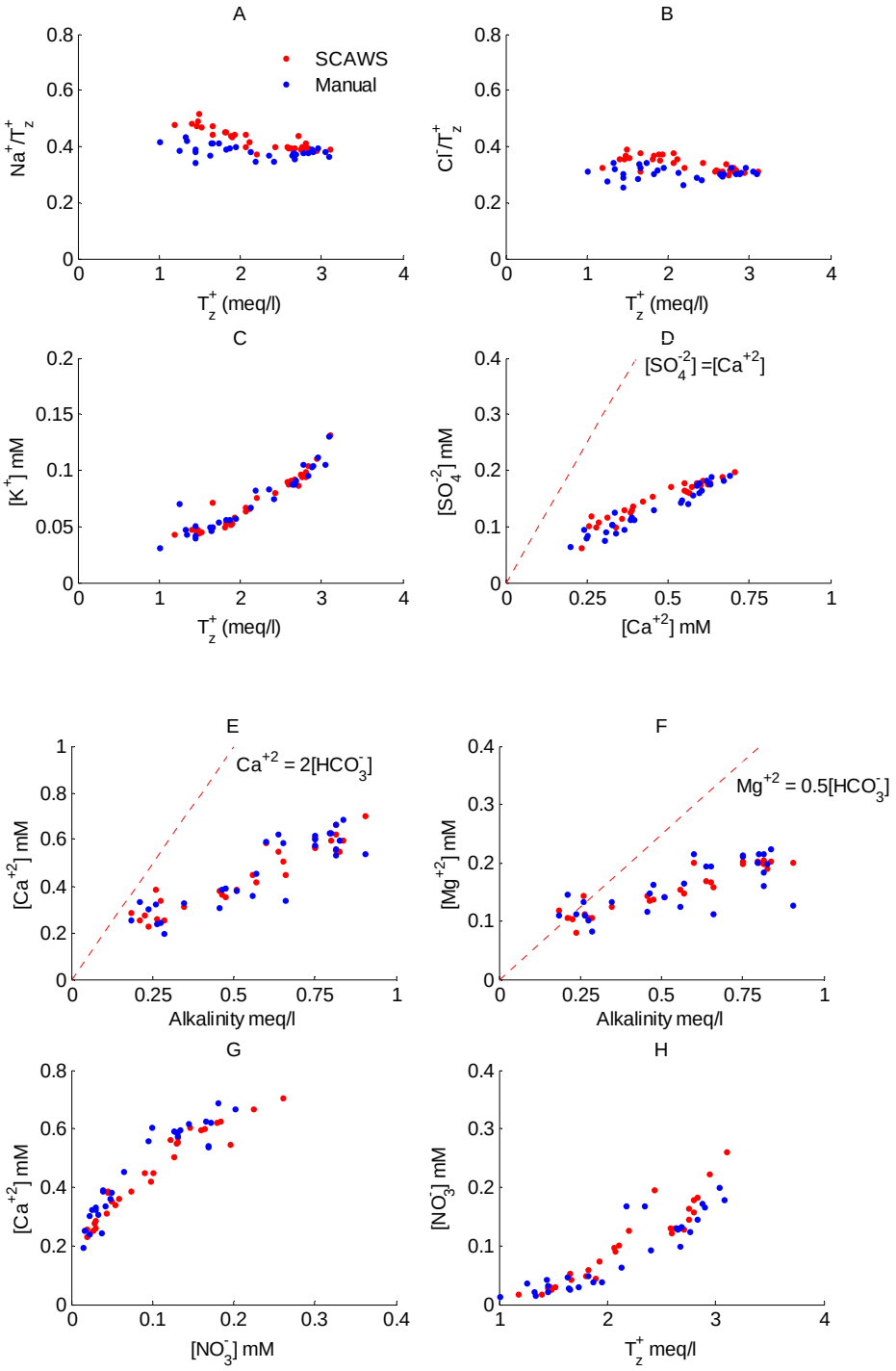


Figure 6-16: Property - property diagrams for the one month river deployment. HCO_3^- is alkalinity values (meq/l). The good correlation ($R^2 = 0.901$) of the Ca+Mg SCAWS values with manual alkalinity values, indicate that the alkalinity values can be used for the evaluation of the SCAWS samples anionic balance. Values have not been corrected for atmospheric input (cyclic salts). Positive correlation between calcium and nitrate (G), suggest the correspondence of nitrate to runoff (Jarvie *et al.*, 2008). This is further supported by the fact that nitrate have a positive correlation with total cations (H). Considering also that phosphate concentration is very low (< 0.2 µM) we can assume that biological activity in the river is controlled by phosphate.

From the property – property diagrams it is also evident that the collected samples provide a realistic picture of the geochemical conditions of Lymington river. Absence of evaporites is indicated by the fact that sodium and chloride ratios to total cations remain fairly constant with increasing concentrations (high T_z^+) (see Figure 6-16 A and B). Potassium presents an opposite behaviour than the one expected from rivers draining marine sediments (see Figure 6-16 C). The Calcium and sulphate data indicate the absence of gypsum or anhydrite, as the data fall far below the $CaSO_4$ dissolution line (see Figure 6-16 D). The same applies for calcium and magnesium plots against alkalinity that fall below the dissolution line, indicating the absence of carbonates (see Figure 6-16 E and F). The correlation that is presented on the lower part of the line is probably associated to carbonate that overlays the river bed. Nitrate concentrations (see Figure 6-16 G and H) present a good correlation with both calcium and the total cationic charge, which indicates that nitrate is not controlling biological activity in Lyminghton river. Further information on nitrate behaviour is obtained from the relationship between the river's flow rate and the concentration (see below).

Cyclic salt correction (Stallard and Edmond, 1981, 1983) can give more information on the rivers water geochemistry. Correction can be based on the ratio that chloride or sodium have to solutes in seawater and then subtract this fraction from the actual concentration of the solute in river water (Stallard and Edmond, 1981). A more realistic picture of the contribution of cyclic salts to a rivers dissolved load can be obtained if the ratios of chloride or sodium to other solutes are calculated from (marine) rain water samples (Stallard and Edmond, 1981; Negrel and Roy, 1998; Roy *et al.*, 1999). For this study we collected rain water (two samples at different days. Samples were collected with corrugated plates that were rinsed before with deionized water) and analysed it for major anions and cations (DX500 IC system) but results between the samples present significant differences that are reflected on the ratios (See Table 6-8). These differences may be related to the fact that the two samples were collected during different conditions. More specifically the first sample was collected after a dry period of approximately 20 days, while the second sample was collected after approximately 5 days of rain. Blank samples (deionized water that was passed through the collection scheme) did not indicate any contamination from either the collection bottles, or the collection scheme.

	Concentrations in μM						
	Cl^-	SO_4^{-2}	NO_3^-	Na^+	K^+	Mg^{+2}	Ca^{+2}
30/04/08	17.6	6.6	14.0	17.1	2.4	2.7	14.5
09/07/08	16.4	1.6	4.4	28.3	4.4	1.8	8.0
Seawater (mM)	*558*	*28.9*	-	*479*	*10.4*	*54.3*	*10.5*
	Ratios X/Cl						
	Cl^-	SO_4^{-2}	NO_3^-	Na^+	K^+	Mg^{+2}	Ca^{+2}
30/04/08	1	0.38	0.80	0.97	0.13	0.157	0.827
09/07/08	1	0.096	0.27	1.72	0.27	0.117	0.49
mean	1	0.24	0.53	1.35	0.20	0.13	0.66
Seawater	*1*	*0.0518*	-	*0.86*	*0.0186*	*0.10*	*0.0188*

Table 6-8: Concentration of major anions and cations in rainwater, and ratios of solute (X) to chloride. See section 4.3.3.1 for the analytical errors of the DX500 system. Seawater values were obtained from (Berner and Berner, 1996)

The interesting point of the rain water data is that chloride values are similar, in contrast to the other solutes. However cyclic salt correction using the rain water ratios from Table 6-8 does not provide coherent and realistic data (negative values of solutes). For this reason we will assume that chloride in rain water do not experience significant alteration from atmospheric processes or inputs from anthropogenic sources (in contrast to studies that use sodium ratios in rainwater to perform the cyclic salt correction (Negrel and Roy, 1998; Roy *et al.*, 1999), because of the increasing contribution of anthropogenic activities to chloride concentrations in rainwater) and assume that all the chloride in rain water are marine derived. In addition to the above assumption, we assume that all the chlorides in Lymington River are derived from rain waters (hence marine derived chloride as there are no evaporites in the drainage basin of the river). For this reason correction for cyclic salts is based on the sea water ratio of chloride to the rest of the major ions.

The molar ratios of chloride to the rest of the conservative solutes are taken from Berner and Berner (1996).

The "cyclic salt corrected" concentrations (X^*) are calculated from equation 6-4.

$$X^* = X - R \cdot [Cl^-]_{RW} \qquad \textbf{6-4}$$

where X is the concentration of solute in river water, R the ratio for the respective solute, and $[Cl^-]_{RW}$ is the chloride concentration in river water. Tabulated data are presented in the APPENDIX. For each sampling method we used the corresponding values. Therefore chloride concentrations of SCAWS samples were used for the correction of SCAWS samples and likewise for manual samples. Results from the cyclic salt correction are presented in Figure 6-17.

Cyclic salt correction indicates the significance of rain deposition for sodium and magnesium (Figure 6-17). Corrected values present similar patterns for both sampling methods.

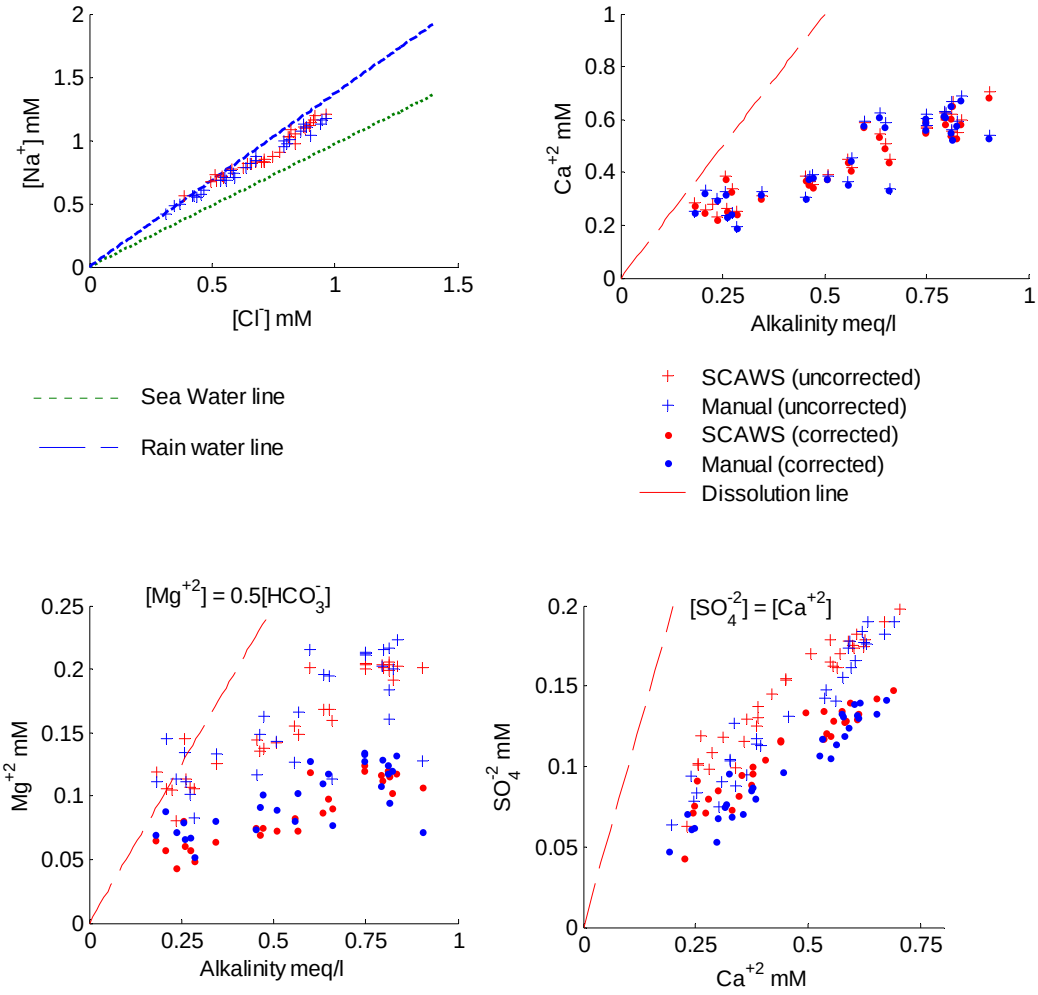


Figure 6-17: Sodium and chloride from rainwater and property –property diagrams after cyclic salt correction. The rain water line was calculate using the Na:Cl of "Southampton area" rain water that was collected and analysed on IC (see Table 6-8).

A cationic ternary diagram is presented in Figure 6-18, where it is evident the contribution of alkalis (predominantly Na^{+}) and Ca^{+2} on the cationic charge.

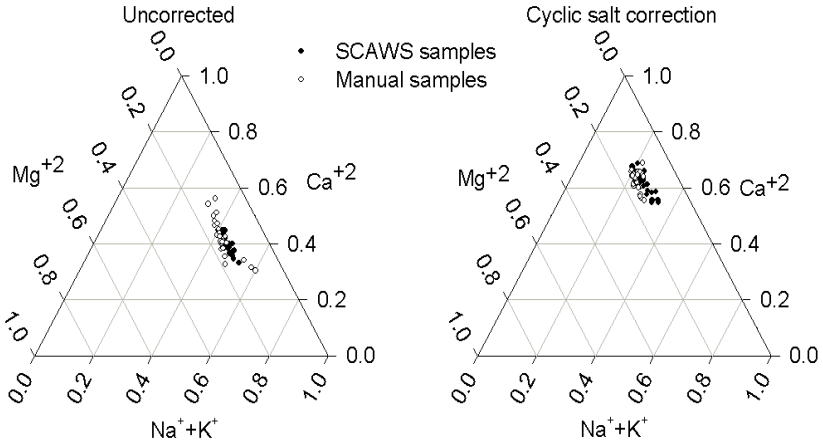


Figure 6-18: Ternary diagram for the major cations during the one month river deployment. Values for both sampling methods fall close to the Na+K and Ca^{+2} apexes, indicating the significance of cyclic salts. This is supported on the cyclic salt correction diagram, where the Ca^{+2} contribution to the cationic charge has increased and Na contribution has decreased. The diagrams were produced using equivalents of each solute.

Further information can be extracted from the relationship between the average river discharge and the concentrations of the solutes (see Figure 6-19). Regression parameters are presented in Table 6-9.

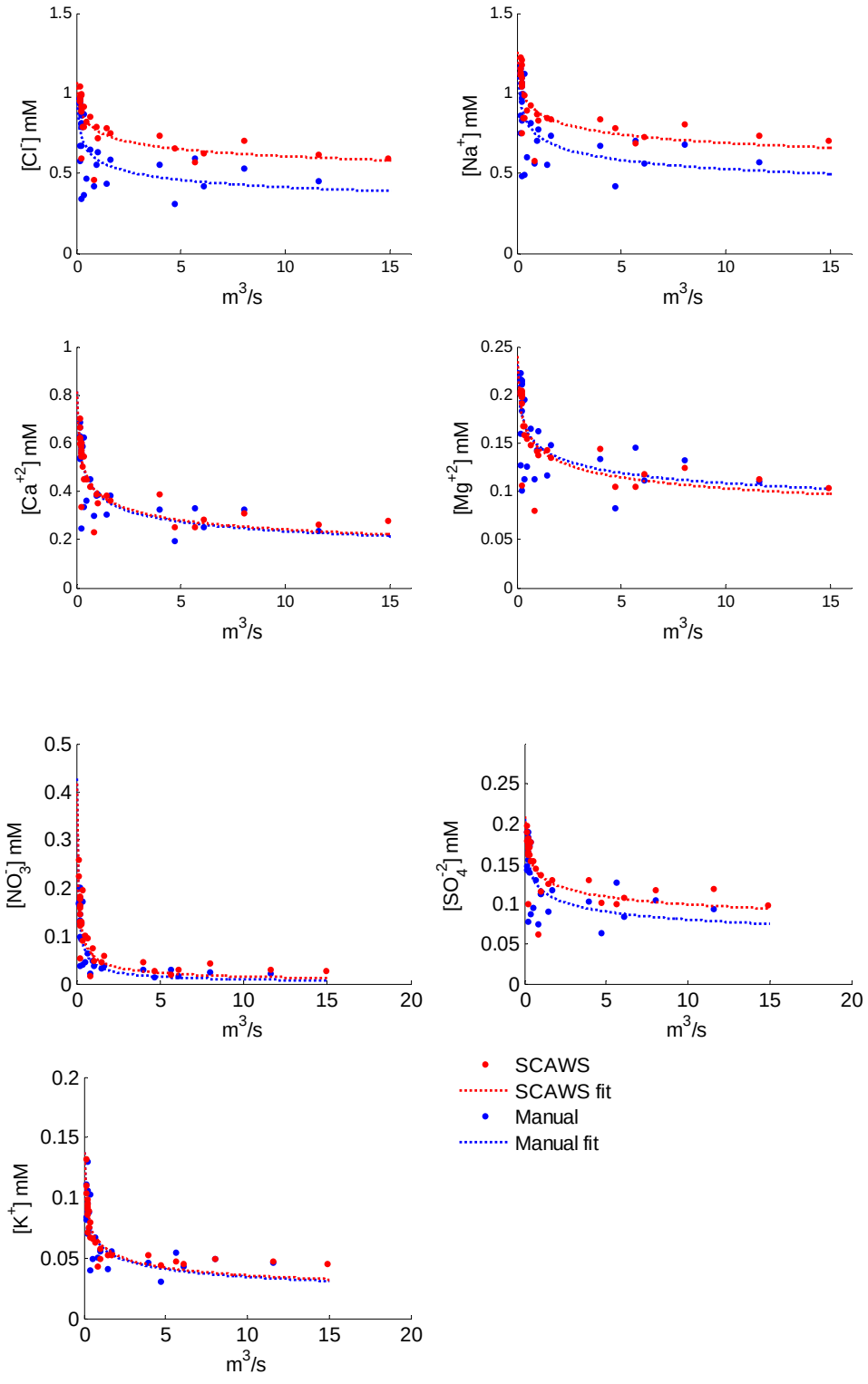


Figure 6-19: River discharge (Q) and concentration (C) relationship. Diagrams, indicate that concentrations follows a $C=a \cdot Q^{-b}$ relationship with flow rates. Regression parameters a, b, R^2 are presented in Table 6-9.

	SCAWS			Manual		
Solutes	a	b	R^2	a	b	R^2
Cl^-	0.766±0.042	0.102±0.040	0.58	0.588±0.072	0.154±0.082	0.39
Na^+	0.882±0.047	0.107±0.035	0.61	0.738±0.080	0.147±0.073	0.43
Ca^{+2}	0.398±0.031	0.217±0.052	0.78	0.391±0.030	0.222±0.076	0.65
Mg^{+2}	0.146±0.010	0.151±0.046	0.66	0.148±0.015	0.135±0.068	0.42
NO_3^-	0.059±0.019	0.594±0.200	0.77	0.044±0.021	0.690±0.269	0.74
SO_4^{-2}	0.135±0.009	0.134±0.046	0.59	0.11±0.013	0.169±0.076	0.48
K^+	0.062±0.005	0.241±0.054	0.80	0.067±0.008	0.247±0.085	0.65

Table 6-9: Regression parameters for the river discharge - concentration relationship. Regressions were performed using MATLAB regression package (non-linear least squares regression) and values are within 95% confidence limits.

As far as it concerns the relationship between concentration and flow, major anions and cations present a well – defined dilution with flow, which follows a $C=a\cdot Q^{-b}$ relationship. This model is suggested also in other rivers (Roy *et al.*, 1999; Chen *et al.*, 2002; Jarvie *et al.*, 2008), and illustrates the dilution of solutes when flow rate is increasing. The nitrate profile indicates that anthropogenic related nitrate was not significant during the deployment period (Seine River that has significant contribution of nitrate from anthropogenic sources (Roy *et al.*, 1999) presents a different nitrate profile). Comparing with other similar size catchments nitrate data (concentrations and flow rate profiles) are considered medium and there are no indications of significant anthropogenic input during the deployment period (Neal and Robson, 2000; Jarvie *et al.*, 2005; Jarvie *et al.*, 2008).

The fluxes of each solute, in mole/s and for each sampling method, during the deployment period are presented in Figure 6-20. The fluxes were calculated from equation 6-5.

$$J_{k\,i}\,(moles/d) = C_i(moles/m^3)\cdot Q(m^3/d) \qquad \textbf{6-5}$$

Where J_{ki} is the flux of solute (i) in mole/s, C_i the concentration of solute (i) in mole/l at day k, and Q is the average daily river discharge in m^3/d (see Figure 6-5). Equation 6-5 provides the daily average flux of each solute. The total flux of each solute ($J_{T\,i}$) is provided by equation 6-6.

$$J_{T\,i}\,(moles) = \sum_{k=1}^{n} J_{k\,i} \qquad \textbf{6-6}$$

Where n is the number of the deployment days (for our case n=30).

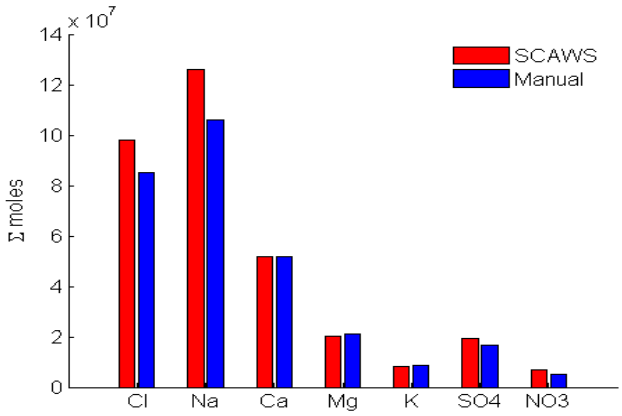


Figure 6-20: Comparison of fluxes during the one month river deployment.. The fluxes were calculated using the daily average discharge rates. Chloride and sodium fluxes are calculated using values that were corrected from rhodamine contamination. Cyclic salt correction was not applied on the concentration values.

Fluxes of solutes during the deployment period are presented in Figure 6-20. From this diagram it is evident that chloride and sodium present significant differences (>10%) between the two sampling methods. Values from the SCAWS samples are corrected from the rhodamine contribution; therefore we believe that differences are real. This is more supported by the fact that nitrate and sulphate fluxes present differences between the two sampling methods, even though samples were not "contaminated". This brings up the question whether fluxes of dissolved matter of river water that are estimated from even daily samples are accurate. Results have been extracted from just a one month deployment period. Coherent and definite answer to the above question and whether these differences are representative can only be obtained if the sampler is deployed for longer period and with a tracer that does not contaminate the samples.

Overall, the geochemical trends that are produced from the SCAWS samples are very similar to the ones produced from the manual samples.

6.4 Conclusions

Overall the outcomes from the river deployments can be considered positive. Both deployments proved that the SCAWS is a reliable and useful water sampler. Before the one month deployment the SCAWS (either MKI or MKII) has not been deployed in aquatic environments that experience significant short term variations in environmental conditions.

The basic design of the SCAWS is very robust and can sustain water sampling even under very hostile conditions. The most important is that the sampling – chemical performance of the sampler was very encouraging. For major anions and cations sampling reliability is high (proved in both

river deployments). This is further supported by the basic geochemical analysis of the retrieved data and the generally good agreement of results that were produced by both sampling methods.

The concept of time stamping of the sampling tube over a one month deployment period in a natural (hostile) environment was also proved. Samples deduced from the time stamping system, had small differences from theoretical segmentation profiles. However the contribution of rhodamine on chloride and sodium concentrations is significant (>10%), which indicates the need to use tracers that present the same advantages with rhodamine (easy detection) but do not contribute on concentrations of any solute of interest.

Statistical analysis and comparison of the results produced from the two sampling methods were used to identify the reliability of the sampler. Such a comparison is inherently difficult as it is difficult to estimate (both statistically and practically) the inherent errors of the two methods. However, what is evident from the one month deployment is that the aquatic picture of the deployment site was characterized adequately, with the data that were extracted from the samples collected from both methods. Significant changes (flood – dilution) were sampled reliably, which proves the SCAWS (and consequently the osmo sampling technology) can become a valuable tool for water sampling and monitoring of aquatic environments.

Considering the significant logistical advantages that an autonomous, robust and high sampling resolution water sampler presents over conventional methods, it is easy to understand how useful the SCAWS can be on environmental and geochemical research.

Potential applications of the SCAWS and insights of how the sampler can be part of integrated geochemical research projects or environmental monitoring and management's schemes are presented in chapter 7.

7 Conclusion

7.1 Objectives

The main objectives of the project were to design, manufacture and deploy a continuous autonomous water sampler that is based on the principle of OsmoSamplers. From what has been presented in chapters 2, 5 and 6, it is evident that the main target was achieved. Main comments on each one of the above targets are presented in sections 7.1.1 and 7.1.3.

7.1.1 Design – Engineering - Development

The basic design follows the design principle of existing OsmoSamplers (see chapters 2 and 3). During the development stage the challenges that are associated with such samplers were identified and studied (see chapter 2). It was recognised that deployment of the sampler in different aquatic environments will be even more challenging. The engineering approach that was followed in order to address these challenges was aiming to increase the sampler's versatility and ability to be deployed in various aquatic environments, but at the same time not hinder its simple and robust character. From what was presented it is clear that both the time stamping system and the custom filtering device need to be improved (see section 7.3). However, it should be noted that the principle behind both the time stamping system and the filtration device has been proved and results from laboratory tests and field deployments, indicate that they can be used on the SCAWS. The challenges associated with them, are related to the optimization of the auxiliary equipment that is necessary for their operation (electronic circuit, batteries).

The design of the SCAWS proved very robust and helped the sampler to operate even during very hostile conditions. Overall the SCAWS performed well, and it was proved that it is a reliable sampler.

7.1.2 Analytical techniques

As was mentioned in chapter 4, the selection of the analytical techniques is very important for osmo samplers and the SCAWS. The reasons were explained in chapter 4. Analysis of river water samples was less challenging than analysis of sea waters. Hence, the results are more accurate for the river water samples. The techniques served well for the purpose of this project, which was mainly to evaluate the sampler. Development of more sophisticated and customized analytical protocols on the SCAWS, and consideration of different analytical methods, should be considered for future applications of the sampler. Some of them are discussed in section 7.2.2.

7.1.3 Deployments

7.1.3.1 Marine deployments

The marine deployments in NOCS floating pontoon, gave a clear picture that the SCAWS can operate autonomously in a natural environment. The results from the chemical analysis of the collected samples and the comparison with manually collected samples, proved the reliability of the sampler. The marine deployments were short and in an environment without any particular scientific (marine geochemistry – environmental monitoring) interest. During the three marine deployment periods there were no significant changes in the physical and chemical conditions, so it was not possible to evaluate the sampler's ability to address this issue. The chemical analysis results from the marine deployments showed good agreement between the SCAWS samples and the manually collected samples, especially for conservative elements, but for nitrate and trace metals, the results are more ambiguous. This is associated with the analytical techniques that were used. In such cases both the sampler and the analytical techniques need to be optimised for the purposes of such applications.

7.1.3.2 River Deployments

The rationale behind the river water deployments is discussed in chapter 6. In this case, in addition to evaluating the performance of the SCAWS, we were also able to study fundamental geochemical processes. Results for a one month continuous sampling indicate that the sampler can perform reliably. The concentrations of analytes from the two sampling methods (SCAWS – Manual) are very similar for most analytes. During the deployment period environmental conditions changed significantly. These changes were reflected in the water chemistry and they were captured accurately and reliably by the SCAWS. Determination and calculation of basic geochemical indexes were also realistic using results from the SCAWS samples, and in some cases were more representative than those obtained from the manually collected samples. The most interesting evidence that may indicate the advantage of the SCAWS over conventional sampling are extracted from the flow rates and the elemental fluxes that are calculated from data derived from either sampling method.

The SCAWS, like all water samplers, should be considered as a tool, which is used within an integrated hydrogeochemical scientific project or a water monitoring/management system. Such systems/projects include the collection of samples, the analysis of samples and the interpretation of the results. As stated previously (chapters 5 and 6) the SCAWS, can be an important asset for an integrated geochemical research project and water management/monitoring schemes.

7.2 Future directions

7.2.1 Optimization

From all the deployments of the SCAWS it was obvious that there is both the necessity and the ability to improve the sampler. Some ideas have already been mentioned (see section 3.4). After the deployments of the sampler and the identifications of the advantages and the challenges that are associated with the SCAWS, the following should be considered, in order for the SCAWS to become a more powerful and more competitive water sampler:

- *Optimization of the time stamping system:* the application of rhodamine 6G needs to be reconsidered, particularly when spectrophotometric/ colorimetric analytical techniques are used. This is important for seawater deployments where nutrients are determined spectrophotometrically (e.g. Auto - Analyzer). In addition the contribution of the rhodamine on sodium and chloride concentrations presents questions whether rhodamine should be used for river deployments as well. We believe that for river (shallow water) applications the injection of an inert gas instead of a fluid may improve the sampler's performance significantly. Development of this system is a priority for future shallow water deployments of the sampler.
- *Acid - preservative addition:* Results for trace metals indicate the necessity to include an acid addition device. Depending on the project this can be achieved either with the addition of a second smaller osmotic pump, or using hydrostatics and flow restrictors to ensure constant flow of the preservative to the sample. Preservative addition will provide the opportunity to use the SCAWS for different sampling applications (e.g. phytoplankton with lugol's solution).
- *Minimization:* The parts of the SCAWS that can be minimized are the custom made filtering device and the associated renewing mechanism (see section 3.2.4) and the case of the solenoid pump. For the filtering device, minimization will also reduce the amount of power that is required to renew the filter. This will increase the operational life of the SCAWS and make it more attractive and versatile. Minimization of the pumps/valves case depends on the size of the solenoid pumps that will be used. The main concern is the power requirements of the pump and selection should be based on minimal power consumption.
- *Customization:* The versatile nature of the SCAWS, renders it suitable for a variety of applications. With the appropriate modifications, the SCAWS can be applied to any aquatic environment. Modifications might include:
    - Preservative addition depending on the analytical needs (HCl for trace metals, H_2SO_4 for NO_3^-, lugol for phytoplankton)
    - For applications in deep marine environments (>50 m) the filtration system is not required, as the suspended matter concentration in these environments is low. Also the fact that in such application the sample will be alongside other monitoring

sensors, and in particular temperature sensors, indicates that the time stamping device is not required, because the sampling segmentation profile can be deduced from the temperature flow rate relationship. Therefore for such applications the use of just the osmo pump and the sampling tube, equipped with a preservative addition system, will be adequate.

7.2.2 Analytical techniques

As has been mentioned in chapter 4 and in section 7.2, analytical techniques are very important part of the SCAWS "package". The rationale behind the analytical techniques and protocols that were used for the project was presented in chapter 4. These techniques served the purposes of the project, but it was evident from the deployments that there is room for improvement in the analytical protocols (e.g. special considerations for trace metals analysis). Alternative analytical techniques should also be considered that will allow determination of different analytes (e.g. modify the flow injection autoanalayzers for nutrient determination, but also for trace metals analysis (Blain and Triguer, 1995; Wu and Boyle, 1997; Bowie *et al.*, 2002; Gardolinski *et al.*, 2002; Gray *et al.*, 2006)).

Future deployments of the SCAWS should incorporate determination of silicate (essential parameter for both marine and river waters). For river water applications, determination of alkalinity on "osmo" samples, using micro – electrodes (see section 4.5) should also be considered.

7.2.3 Integrated research

The work outlined in the in the previous chapters has confirmed that OsmoSamplers are reliable and efficient sampling devices for obtaining long term (time series) chemical records (see chapter 2 and chapter 6). However, from the literature it is not evident that osmo samplers were part of research that apart from temporal resolution, addresses the spatial aspect of changes. Integrated environmental management and hydrogeochemical research requires observations to cover as many dimensions as possible; therefore the need to record changes in space is essential. Simultaneous use of multiple SCAWSs deployed within a wider area of an aquatic environment, can provide the means to obtain high temporal resolution chemical records, combined with spatial coverage. This application is more feasible in terrestrial or coastal aquatic environments were processes are easier to constrain e.g. end member points, agricultural input, weathering intensity of an area with specific geological characteristics (carbonates, aluminosilicates etc.). In addition the logistical and financial requirements are more feasible on terrestrial environments. Potential "platforms" for such projects can be small research catchments (see section 1.1). Most of these catchments are already equipped with monitoring equipment that can work in parallel with osmo samplers. Application of osmo samplers in these environments, can replace frequent conventional sampling, which will affect the

operational cost of the research catchment/project. The fact also that the cost of osmo samplers is much lower than many automated samplers and monitoring schemes and require far less maintenance, renders them very competitive devices for sampling applications.

Osmo samplers (and the SCAWS), are generic versatile samplers that can be used in a variety of aquatic environments were sampling frequency is legally required. Sampling is continuous and regardless of the environmental conditions, fluid will be sampled. Therefore, potential use in landfills or wastewater streams from industrial facilities, are a few of the sampler's application fields.

Coupling osmo samplers with other monitoring and sampling techniques and integrating them in water research and management systems can only provide a better picture of aquatic environments.

8 References – Bibliography

Adamski, R. P. & Anderson, J. L. (1983), Solute concentration effect on osmotic reflection coefficient. *Biophys. J.,* 44**,** 79-90.

Alewell, C., Lischeid, G., Hell, U. & Manderscheid, B. (2004), High temporal resolution of ion fluxes in semi-natural ecosystems - gain of information or waste of resources? *Biogeochemistry,* 69**,** 19-35.

Altisan, I. A. R. (2006) Effects of light and nutrient gradients on the taxonomic composition, size structure and physiological status of the phytoplankton community within a temperate eutrophic estuary. *School of Ocean and Earth Sciences.* Southampton, University of Southampton.

Bate, H., Rowlands, S., Sirs, J. A. & Thomas, H. W. (1969), The dispersion of diffusible ions in fluid flow through a cylindrical tube. *Journal of Physics D: Applied Physics***,** 1447.

Bates, B. C., Kundzewicz, Z. W., Wu, S. & Palutikof, J. P. (2008), Climate Change and Water. *Technical paper of the IPPC* 210.

Bell, J., Betts, J. & Boyle, E. (2002), MITESS: a moored in situ trace element serial sampler for deep-sea moorings. *Deep-Sea Research I,* 49(11)**,** 2103-2118.

Berner, E. K. & Berner, R. A. (1996), *Global environment : water, air and geochemical cycles,* Upper Saddle River, NJ, Prentice-Hall.

Berner, R. A. & Rao, J.-L. (1994), Phosphorus in sediments of the Amazon River and estuary: Implications for the global flux of phosphorus to the sea. *Geochimica et Cosmochimica Acta,* 58**,** 2333.

Blain, S. & Triguer, P. (1995), Ironn (II) and iron(III) determination in sea water at the nanomolar level with selective on-line preconcentration and spectrophotometric determination. *Analytica Chimica Acta,* 308**,** 425-432.

Bowie, A. R., Achterberg, E. P., Sedwick, P. N., Ussher, S. & Worsfold, P. J. (2002), Real-Time Monitoring of Picomolar Concentrations of Iron(II) in Marine Waters Using Automated Flow Injection-Chemiluminescence Instrumentation. *Environmental Science & Technology,* 36**,** 4600-4607.

Brewer, P. G. & Riley, J. P. (1965), The automatic determination of nitrate in sea water. *Deep Sea Research and Oceanographic Abstracts,* 12**,** 765-772.

Bricker, O. P., Paces, T., Johnson, C. E. & Sverdrup, H. (1994), Weathering and Erosion Aspects of Small Catchment Research. In Moldan, B. & Cerny, J. (Eds.) *Biogeochemistry of Small Catchments: A Tool for Environmental Research* Chichester, John Willey & Sons Ltd.

Burton, J. D. (1980), *The Solent Estuarine System : an assessment of present knowledge,* Swindon, Natural Environment Research Council.

Carson, B., Kastner, M., Bartlett, D., Jaeger, J., Jannasch, H. & Weinstein, Y. (2003), Implications of carbon flux from the Cascadia accretionary prism: results from long-term, in situ measurements at ODP Site 892B. *Marine Geology,* 198**,** 159-180.

Chakrapani, G. J. (2005), Major and trace element geochemistry in upper Ganga river in the Himalayas, India. *Environmental Geology,* V48**,** 189-201.

Chapin, T. P., Caffrey, J. M., Jannasch, H. W., Coletti, L. J., Haskins, J. C. & Johnson, K. S. (2004), Nitrate sources and sinks in Elkhorn Slough, California: Results from long-term continuous in situ nitrate analyzers. *Estuaries,* 27**,** 882-894.

Chapin, T. P., Jannasch, H. W. & Johnson, K. S. (2002), In situ osmotic analyzer for the year-long continuous determination of Fe in hydrothermal systems. *Analytica Chimica Acta,* 463**,** 265.

Chen, J., Wang, F., Xia, X. & Zhang, L. (2002), Major element chemistry of the Changjiang (Yangtze River). *Chemical Geology,* 187**,** 231-255.

Christophersen, N., Clair, T. A., Driscoll, C. T., Jeffries, D. S., Neal, C. & Semkin, R. G. (1994), Hydrochemical Studies. In Moldan, B. & Cerny, J. (Eds.) *Biogeochemistry of Small Catchments: A Tool for Environmental Research.* Chichester, John Willey & Sons Ltd.

Collins, M. & Ansell, K. (2000), *Solent Science - a review. (Proceedings of Solent Science Conference, Southampton, 29 September 2000),* Amsterdam, Elsevier Science.

Conte, M. (1997), The Oceanic Flux Program. *Oceanus,* 40(2)**,** 15-19.

Crank, J. (1956), *The Mathematics of diffusion,* Oxford, Clarendon Press.

Dahlqvist, R., Zhang, H., Ingri, J. & Davison, W. (2002), Performance of the diffusive gradients in thin films technique for measuring Ca and Mg in freshwater. *Analytica Chimica Acta,* 460**,** 247-256.

Deuser, W. G., Muller-Karger, F. E. & Hemleben, C. (1988), Temporal variations of particle fluxes in the deep subtropical and tropical North Atlantic: Eulerian versus Lagrangian effects. *Journal of Geophysical Research,* 93(C6)**,** 6857-6862 & plates.

Deuser, W. G. & Ross, E. H. (1980), Seasonal change in the flux of organic carbon to the deep Sargasso Sea. *Nature,* 283**,** 364.

Dick, E. M. (1996), Automatic Water and Wastewater Sampling. In Keith, L. H. (Ed.) *Principles of Environmental Sampling.* Washington D.C.

Dočekalová, H. & Divis, P. (2005), Application of diffusive gradient in thin films technique (DGT) to measurement of mercury in aquatic systems. *Talanta,* 65**,** 1174-1178.

Drever, J. I. (1988), *The geochemistry of natural waters,* Englewood Cliffs, N.J., Prentice Hall.

Eaton, A. D., Franson, M. A. H., American Public Health Association., American Water Works Association. & Water Environment Federation. (2005), *Standard methods*

for the examination of water & wastewater, [Washington, D.C.], American Public Health Association.

Edmond, J. M., Boyle, E. A., Grant, B. & Stallard, R. F. (1981), The Chemical Mass Balance In The Amazon Plume I - The Nutrients. *Deep-Sea Research Part A-Oceanographic Research Papers,* 28**,** 1339-1374.

Edmond, J. M., Palmer, M. R., Measures, C. I., Brown, E. T. & Huh, Y. (1996), Fluvial geochemistry of the eastern slope of the northeastern Andes and its foredeep in the drainage of the Orinoco in Colombia and Venezuela. *Geochimica Et Cosmochimica Acta,* 60**,** 2949-2976.

Edmond, J. M., Palmer, M. R., Measures, C. I., Grant, B. & Stallard, R. F. (1995), The Fluvial Geochemistry And Denudation Rate Of The Guayana Shield In Venezuela, Colombia, And Brazil. *Geochimica Et Cosmochimica Acta,* 59**,** 3301-3325.

Fang, T.-H. (1995) Studies of the behaviour of trace metals during mixing in some estuaries of the Solent region. University of Southampton, Dept. of Oceanography.

Fones, G. R., Davison, W., Holby, O., Jorgensen, B. B. & Thamdrup, B. (2001), High-resolution metal gradients measured by in situ DGT/DET deployment in Black Sea sediments using an autonomous benthic lander. *Limnology and Oceanography,* 46**,** 982-988.

Garbarino, J. R., Kanagy, L.K., & Cree, M. E. (2006) Determination of elements in natural-water, biota, sediment, and soil samples using collision/reaction cell. *Techniques and Methods, book 5, sec. B, chap. 1, 88 p.*, U.S. Geological Survey.

Gardolinski, P., David, A. R. J. & Worsfold, P. J. (2002), Miniature flow injection analyser for laboratory, shipboard and in situ monitoring of nitrate in estuarine and coastal waters. *Talanta,* 58**,** 1015-1027.

Garrels, R. M. & Mackenzie, F. T. (1971), *Evolution of sedimentary rocks*, W.

Gibbs, R. J. (1970), Mechanisms Controlling World Water Chemistry. *Science,* 170**,** 1088-1090.

Gjerde, D. T., Fritz, J. S. & Schmuckler, G. (1979), Anion Chromatography With Low-Conductivity Eluents. *Journal of Chromatography,* 186**,** 509-519.

Golshani, A. (1998) Monitoring chemical variations with OsmoSamplers in estuarine systems: Elkhorn Slough case study.

Gray, S., Hanrahan, G., Mckelvie, I., Tappin, A., Tse, F. & Worsfold, P. (2006), Flow analysis techniques for spatial and temporal measurement of nutrients in aquatic systems. *Environmental Chemistry,* 3**,** 3-18.

Horlick, G. & Montaser, A. (1998), Analytical Characteristics of ICPMS. In Montaser, A. (Ed.) *Inductively Coupled Plasma Mass Spectrometry.* New York, Wiley - VCH.

Hu, M. H., Stallard, R. F. & Edmond, J. M. (1982), Major Ion Chemistry Of Some Large Chinese Rivers. *Nature,* 298**,** 550-553.

Huh, Y., Chan, L. H. & Edmond, J. M. (2001), Lithium isotopes as a probe of weathering processes: Orinoco River. *Earth And Planetary Science Letters,* 194**,** 189-199.

Huh, Y., Chan, L. H., Zhang, L. & Edmond, J. M. (1998), Lithium and its isotopes in major world rivers: Implications for weathering and the oceanic budget. *Geochimica Et Cosmochimica Acta,* 62**,** 2039-2051.

Hydes, D. (2000), Nutrients in the Solent. In Collins, M. & Ansell, K. (Eds.) *Solent Science - A review (Proceedings in Marine Science).* Amsterdam, Elsevier.

Hydes, D. J. & Wright, P. N. (1999), *SONUS : The Southern Nutrients Study 1995-1997,* Southampton, Southampton Oceanography Centre.

Jannasch, H., Sakamoto, C., Walz, P., Plant, J. & Chapin, T. (1998), Long-term high resolution chemical monitoring with osmotically pumped analyzers and samplers. *Abstracts of Papers of the American Chemical Society,* 216**,** U884-U884.

Jannasch, H. W., Johnson, K. S. & Sakamoto, C. M. (1994), Submersible, osmotically pumped analyzers for continuous determination of nitrate in situ. *Analytical Chemistry,* 66(20)**,** 3352-3361.

Jannasch, H. W., Wheat, C. G., Plant, J. N., Kastner, M. & Stakes, D. S. (2004), Continuous chemical monitoring with osmotically pumped water samplers: OsmoSampler design and applications. *Limnology And Oceanography-Methods,* 2**,** 102-113.

Jarvie, H. P., Haygarth, P. M., Neal, C., Butler, P., Smith, B., Naden, P. S., Joynes, A., Neal, M., Wickham, H., Armstrong, L., Harman, S. & Palmer-Felgate, E. J. (2008), Stream water chemistry and quality along an upland-lowland rural land-use continuum, south west England. *Journal of Hydrology,* 350**,** 215-231.

Jarvie, H. P., Neal, C., Smart, R., Owen, R., Fraser, D., Forbes, I. & Wade, A. (2001), Use of continuous water quality records for hydrograph separation and to assess short-term variability and extremes in acidity and dissolved carbon dioxide for the River Dee, Scotland. *Science Of The Total Environment,* 265**,** 85-98.

Jarvie, H. P., Neal, C., Tappin, A. D., Burton, J. D., Hill, L., Neal, M., Harrow, M., Hopkins, R., Watts, C. & Wickham, H. (2000a), Riverine inputs of major ions and trace elements to the tidal reaches of the River Tweed, UK. *The Science of The Total Environment,* 251-252**,** 55.

Jarvie, H. P., Neal, C., Withers, P. J. A., Wescott, C. & Acornley, R. M. (2005), Nutrient hydrochemistry for a groundwater-dominated catchment: The Hampshire Avon, UK. *Science Of The Total Environment,* 344**,** 143-158.

Jarvie, H. P., Oguchi, T. & Neal, C. (2000b), Pollution regimes and variability in river water quality across the Humber catchment: interrogation and mapping of an extensive and highly heterogeneous spatial dataset. *The Science of The Total Environment,* 251-252**,** 27.

Johnson, C. E., Litaor, M. I., Billet, M. F. & Bricker, O. P. (1994), Chemical Weathering in Small Catchments: Climatic and Anthropogenic Influences. In Moldan, B. &

Cerny, J. (Eds.) *Biogeochemistry of Small Catchments: A Tool for Environmental Research.* Chichester, John Willey & Sons Ltd.

Johnson, N. M., Likens, G. E., Bormann, F. H., Fisher, D. W. & Pierce, R. S. (1969), A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New
Hampshire. . *Water Resources Research,* 5**,** 1353-1363.

Johnson, W. D., Cole, T. J., Johnson, M., Mcpherson, W. P., Muir, G. L. & Szczepanski, R. (1979), Ion balance in water analyses - Effect of added silica on the carbonate-bicarbonate titration. *Australian Journal of Marine and Freshwater Research,* 30**,** 315-323.

Karl, D. M. (1999), The changing sea: long-term biogeochemical variability in the subtropical North Pacific. *Earth System Monitor,* 9(4)**,** 6-12.

Kasnavia, T., Vu, D. & Sabatini, D. A. (1999), Fluorescent Dye and Media Properties Affecting Sorption and Tracer Selection. *Ground Water,* 37**,** 376-381.

Kastner, M., Jannasch, H., Weinstein, Y. & Martin, J. (2000), A new sampler for monitoring fluid and chemical fluxes in hydrologically active submarine environments. *Oceans 2000. Vol. 1. MTS/IEEE Conference Proceedings: Where marine science and technology meet, Providence, RI, 2000.*

Keith, L. H., Patton, G. L., Lewis, D. L. & Edwards, P. G. (1996), Determining what kinds of samples and how many samples to analyze. In Keith, L. H. (Ed.) *Principles of Environmental Sampling, 2nd ed.* Washington, DC, American Chemical Society.

Kirchner, J. W., Feng, X., Neal, C. & Robson, A. J. (2004), The fine structure of water-quality dynamics: the (high-frequency) wave of the future. *Hydrological Processes,* 18**,** 1353-1359.

Kirkwood, D. (1996), Nutrients: practical notes on their determination in sea water. *ICES Techniques in Marine Environmental Sciences,* No.17**,** 25pp.

Li, Y. H. & Gregory, S. (1974), Diffusion of Ions in Sea-Water and in Deep-Sea Sediments. *Geochimica Et Cosmochimica Acta,* 38**,** 703-714.

Macdougall, D., Crummett, W. B. & Et Al. (1980), Guidelines for data acquisition and data quality evaluation in environmental chemistry. *Analytical Chemistry,* 52**,** 2242-2249.

Mauro, A. (1960), Some Properties of Ionic and Nonionic Semipermeable Membranes. *Circulation,* 21**,** 845-854.

Meybeck, M. (1987), Global chemical weathering of surficial rocks estimated from river dissolved loads. *Am J Sci,* 287**,** 401-428.

Meybeck, M. (1998), Man and river interface: multiple impacts on water and particulates chemistry illustrated in the Seine river basin. *Hydrobiologia,* 373-374**,** 1.

Meybeck, M. (2002), Riverine quality at the Anthropocene: Propositions for global space and time analysis, illustrated by the Seine River. *Aquatic Sciences,* 64**,** 376-393.

Meybeck, M. (2003), Global analysis of river systems: from Earth system controls to Anthropocene syndromes. *Philosophical Transactions Of The Royal Society Of London Series B-Biological Sciences,* 358**,** 1935-1955.

Michaels, A. F. & Knap, A. H. (1996), Overview of the US JGOFS Bermuda Atlantic Time-series Study and the Hydrostation S program. *Deep-Sea Research Part Ii-Topical Studies in Oceanography,* 43**,** 157-198.

Miller, J. C. & Miller, J. N. (1988), *Statistics for analytical chemistry. 2nd ed. (Reprinted with corrections 1989)*, Ellis Horwood.

Milliman, J. D., Chen, J. Y., Yang, Z. S. & Ren, M. O. (1983), The Yangtze River - Past, Present and Future. *Oceanus,* 26**,** 20-25.

Moldan, B. & Cerny, J. (Eds.) (1994), *Biogeochemistry of Small Cachments: A Tool for Environmental Research,* Chichester, JOHN WILEY & SONS.

Monbet, P., Mckelvie, I. D. & Worsfold, P. J. (2008), Combined Gel Probes for the In Situ Determination of Dissolved Reactive Phosphorus in Porewaters and Characterization of Sediment Reactivity. *Environmental Science & Technology,* 42**,** 5112-5117.

Morris, A. W. & Riley, J. P. (1963), The determination of nitrate in sea water. *Analytica Chimica Acta,* 29**,** 272-279.

Morris, J. D., Villinger, H. W., A.Klaus, Jannasch, H. W., Davis, E. E., Kastner, M. & Plant, J. N. (2003), 2. CORK-II: Long-Term monitoring of fluid chemistry, fluxes, and hydrology in instrumented boreholes at the Costa Rica Subduction Zone. *Proceeding of the Ocean Drilling Program, Initial reports,* 205(2).

Muller, B., Berg, M., Yao, Z. P., Zhang, X. F., Wang, D. & Pfluger, A. (2008), How polluted is the Yangtze river? Water quality downstream from the Three Gorges Dam. *Science Of The Total Environment,* 402**,** 232-247.

Neal, C. (1999), The water quality functioning of the upper River Severn, Plynlimon, mid-Wales: issues of monitoring, process understanding and forestry. *Hydrology and Earth System Sciences,* 8**,** 521-532.

Neal, C. & Robson, A. J. (2000), A summary of river water quality data collected within the Land-Ocean Interaction Study: core data for eastern UK rivers draining to the North Sea. *The Science of The Total Environment,* 251-252**,** 585.

Negrel, P. & Roy, S. (1998), Chemistry of rainwater in the Massif Central (France): a strontium isotope and major element study. *Applied Geochemistry,* 13**,** 941-952.

Pahl-Wostl, C., Hoff, H., Meybeck, M. & Sorooshian, S. (2002), The role of global change research for aquatic sciences. *Aquatic Sciences,* 64**,** IV-VI.

Palmer, M. R. & Edmond, J. M. (1989), The strontium isotope budget of the modern ocean. *Earth and Planetary Science Letters,* 92(1)**,** 11-26.

Palmer, M. R. & Edmond, J. M. (1992), Controls over the strontium isotope composition of river water. *Geochimica et Cosmochimica Acta,* 56**,** 2099-2111.

Palmer, M. R. & Edmond, J. M. (1993), Uranium In River Water. *Geochimica Et Cosmochimica Acta,* 57**,** 4947-4955.

Peters, A. J., Zhang, H. & Davison, W. (2003), Performance of the diffusive gradients in thin films technique for measurement of trace metals in low ionic strength freshwaters. *Analytica Chimica Acta,* 478**,** 237-244.

Peters, N. E. & Meybeck, M. (2000), Water quality degradation effects on freshwater availability: Impacts to human activities. *Water International,* 25**,** 185-193.

Peters, N. E., Shanley, J. B., Aulenbach, B. T., Webb, R. M., Campbell, D. H., Hunt, R., Larsen, M. C., Stallard, R. F., Troester, J. & Walker, J. F. (2006), Water and solute mass balance of five small, relatively undisturbed watersheds in the US. *Science Of The Total Environment,* 358**,** 221-242.

Pichette, C., Zhang, H. & Sauve, S. (2009), Using diffusive gradients in thin-films for in situ monitoring of dissolved phosphate emissions from freshwater aquaculture. *Aquaculture,* 286**,** 198-202.

Robson, A., Neal, C., Smith, C. J. & Hill, S. (1992), Short-term variations in rain and stream water conductivity at a forested site in mid-Wales -- implications for water movement. *Science Of The Total Environment,* 119**,** 1-18.

Robson, A. J., Neal, C., Hill, S. & Smith, C. J. (1993), Linking variations in short- and medium-term stream chemistry to rainfall inputs -- some observations at Plynlimon, Mid-Wales. *Journal of Hydrology,* 144**,** 291-310.

Roddaz, M., Viers, J., Brusset, S., Baby, P., Boucayrand, C. & Hɪrail, G. (2006), Controls on weathering and provenance in the Amazonian foreland basin: Insights from major and trace element geochemistry of Neogene Amazonian sediments. *Chemical Geology,* 226**,** 31-65.

Roy, S., Gaillardet, J. & Allegre, C. J. (1999), Geochemistry of dissolved and suspended loads of the Seine River, France: anthropogenic impact, carbonate and silicate weathering. *Geochimica Et Cosmochimica Acta,* 63**,** 1277-1292.

Sabatini, D. A. (2000), Sorption and Intraparticle Diffusion of Fluorescent Dyes with Consolidated Aquifer Media. *Ground Water,* 38**,** 651-656.

Sarin, M. M. & Krishnaswami, S. (1984), Major ion chemistry of the Ganga-Brahmaputra river systems, India. *Nature,* 312**,** 538-541.

Sharples, J. (2000), Water Circulation in Southampton Water and the Solent. In Collins, M. & Ansell, K. (Eds.) *Solent Science - A Review (Proceedings in Marine Science).* Amsterdam, Elsevier.

Small, H., Stevens, T. S. & Bauman, W. C. (1975), Novel Ion-Exchange Chromatographic Method using Conductimetric Detection. *Analytical Chemistry,* 47**,** 1801-1809.

Smart & Karunaratne (2002), Characterisation of fluorescence background in dye tracing. *Environmental Geology,* 42**,** 492-498.

Smolders, A. J. P., Hudson-Edwards, K. A., Van Der Velde, G. & Roelofs, J. G. M. (2004), Controls on water chemistry of the Pilcomayo river (Bolivia, South-America). *Applied Geochemistry,* 19**,** 1745-1758.

Solomon, E. A., Kastner, M., Jannasch, H., Robertson, G. & Weinstein, Y. (2008), Dynamic fluid flow and chemical fluxes associated with a seafloor gas hydrate deposit on the northern Gulf of Mexico slope. *Earth And Planetary Science Letters,* 270**,** 95-105.

Soulsby, C., Neal, C., Laudon, H., Burns, D. A., Merot, P., Bonell, M., Dunn, S. M. & Tetzlaff, D. (2008), Catchment data for process conceptualization: simply not enough? *Hydrological Processes,* 22**,** 2057-2061.

Stallard, R. F. & Edmond, J. M. (1981), Geochemistry Of The Amazon .1. Precipitation Chemistry And The Marine Contribution To The Dissolved-Load At The Time Of Peak Discharge. *Journal Of Geophysical Research-Oceans And Atmospheres,* 86**,** 9844-9858.

Stallard, R. F. & Edmond, J. M. (1983), Geochemistry Of The Amazon .2. The Influence Of Geology And Weathering Environment On The Dissolved-Load. *Journal Of Geophysical Research-Oceans And Atmospheres,* 88**,** 9671-9688.

Stallard, R. F. & Edmond, J. M. (1987), Geochemistry Of The Amazon .3. Weathering Chemistry And Limits To Dissolved Inputs. *Journal Of Geophysical Research-Oceans,* 92**,** 8293-8302.

Statham, P. J. (2000), Trace Metals in Waters, Sediments and Biota of the Solent System: A synopsis of Existing Information. In Collins, M. & Ansell, K. (Eds.) *Solent Science - A Revie (Proceedings in Marine Science).* Amsterdam, Elsevier.

Steinberg, D. K., Carlson, C. A., Bates, N. R., Johnson, R. J., Michaels, A. F. & Knap, A. H. (2001), Overview of the US JGOFS Bermuda Atlantic Time-series Study (BATS): a decade-scale look at ocean biology and biogeochemistry. *Deep-Sea Research Part Ii-Topical Studies in Oceanography,* 48**,** 1405-1447.

Stumm, W. & Morgan, J. J. (1996), *Aquatic chemistry : chemical equilibria and rates in natural waters. 3rd ed,* New York, NY, John Wiley & Sons.

Tardy, Y., Bustillo, V., Roquin, C., Mortatti, J. & Victoria, R. (2005), The Amazon. Bio-geochemistry applied to river basin management Part I. Hydro-climatology, hydrograph separation, mass transfer balances, stable isotopes, and modelling. *Applied Geochemistry,* 20**,** 1746-1829.

Taylor, G. (1953), Dispersion of Soluble Matter in Solvent Flowing Slowly through a Tube. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences,* 219**,** 186-203.

Theeuwes, F. (1975), Elementary osmotic pump. *Journal of Pharmaceutical Sciences,* 64**,** 1987-1991.

Theeuwes, F. & Yum, S. I. (1976), Principles of Design and Operation of Generic Osmotic Pumps for Delivery of Semisolid or Liquid Drug Formulations. *Annals of Biomedical Engineering,* 4**,** 343-353.

Van't Hoff, J. (1888), The Function of Osmotic Pressure in the Analogy between Solutions and Gases. *Philosophical Magazine and Journal of Science,* 26.

Vorosmarty, C. J., Fekete, B. M., Meybeck, M. & Lammers, R. B. (2000), Global system of rivers: Its role in organizing continental land mass and defining land-to-ocean linkages. *Global Biogeochemical Cycles,* 14**,** 599-621.

Wheat, C. G., Jannasch, H. W., Kastner, M., Plant, J. N. & Decarlo, E. H. (2003), Seawater transport and reaction in upper oceanic basaltic basement: chemical data from continuous monitoring of sealed boreholes in a ridge flank environment. *Earth And Planetary Science Letters,* 216**,** 549-564.

Wheat, C. G., Jannasch, H. W., Plant, J. N., Moyer, C. L., Sansone, F. J. & Mcmurty, G. M. (2000), Continuous sampling of hydrothermal fluids from Loihi Seamount after the 1996 event. *Journal of Geophysical Research B (Solid Earth),* 105(B8)**,** 19353-19367.

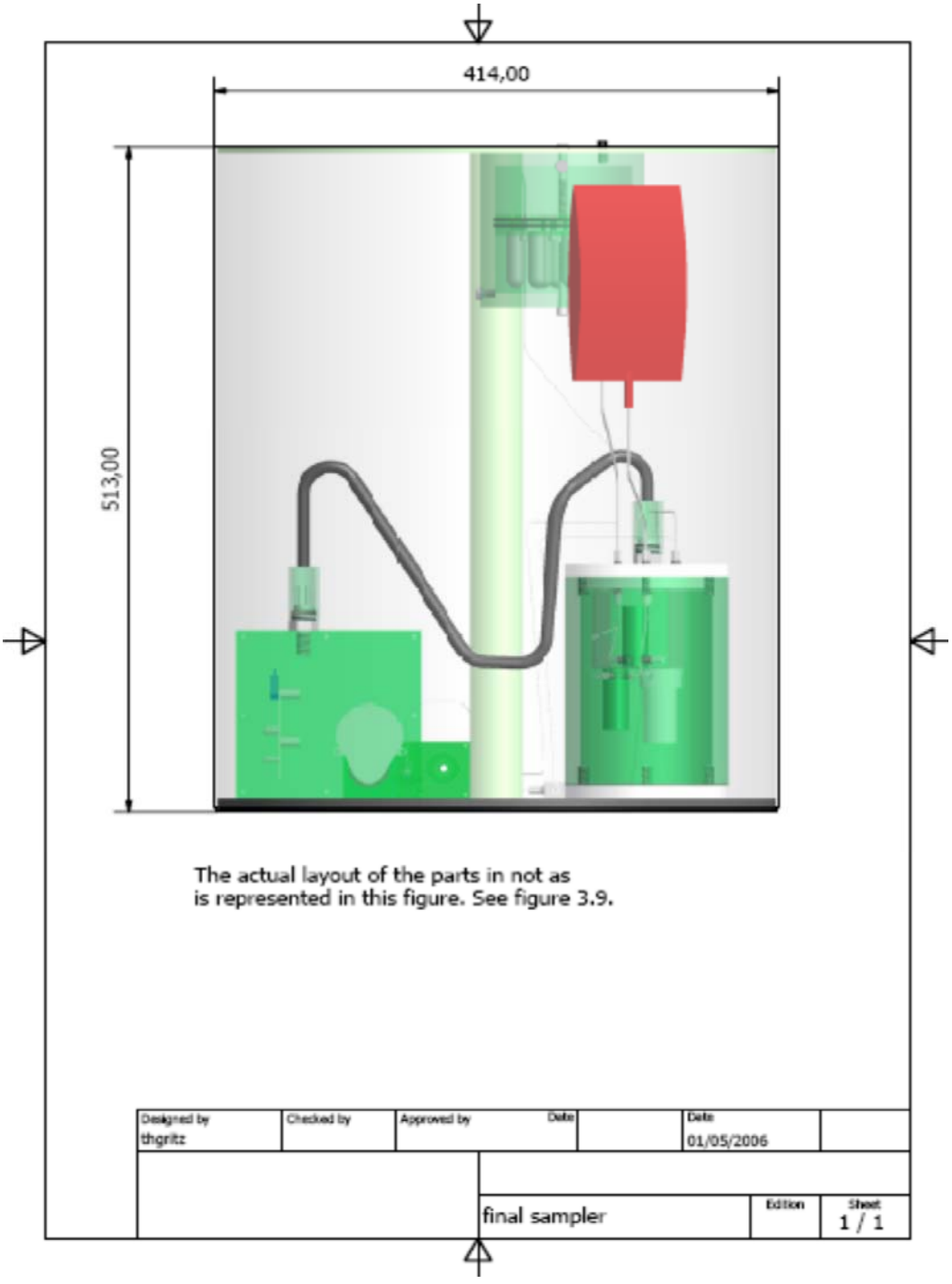
Worsfold, P. J. (2006), Challenges in the determination of nutrient species in natural waters. *Microchimica Acta,* 154**,** 45-48.

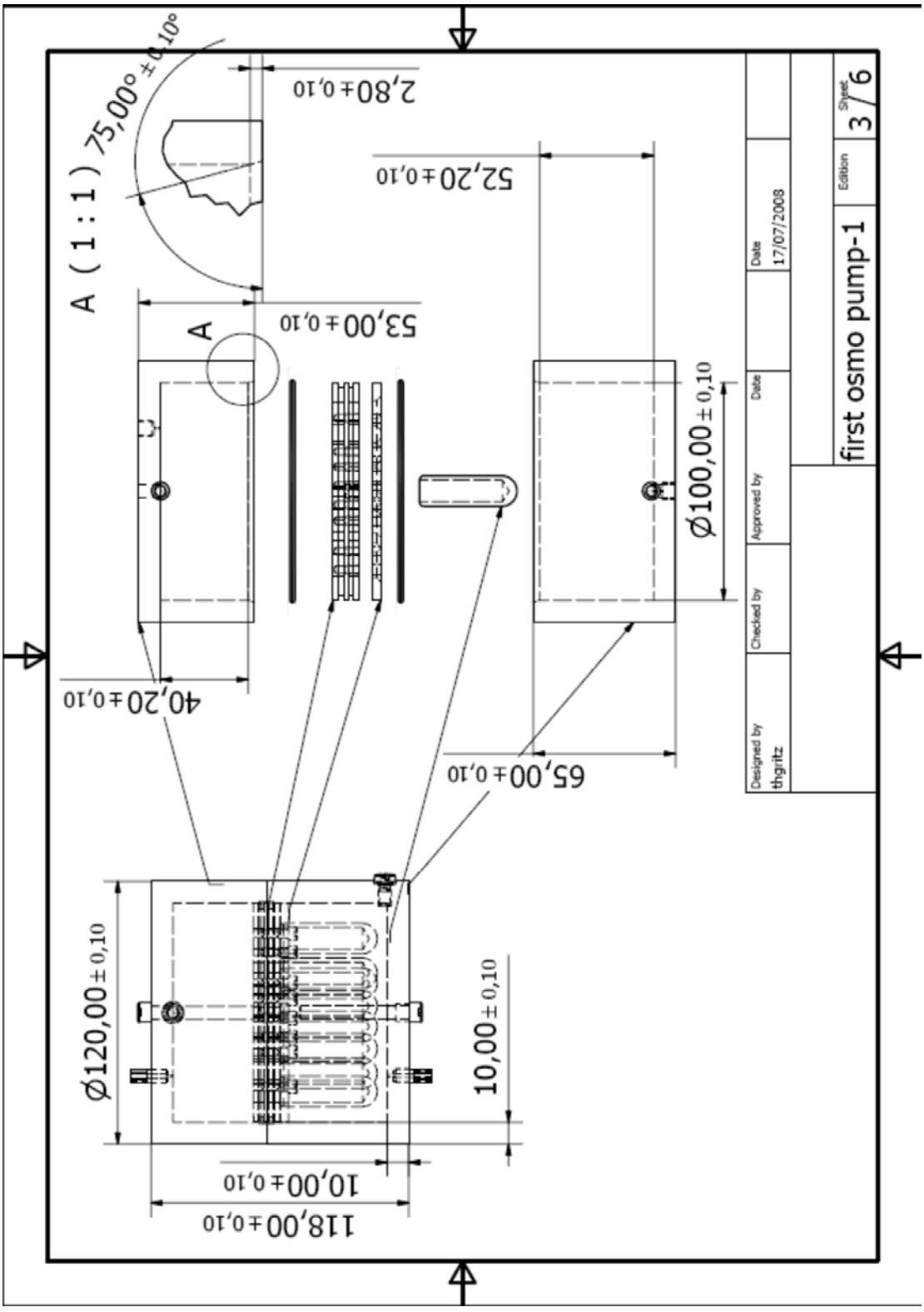
Wu, J. & Boyle, E. A. (1997), Low Blank Preconcentration Technique for the Determination of Lead, Copper, and Cadmium in Small-Volume Seawater Samples by Isotope Dilution ICPMS. *Analytical Chemistry,* 69**,** 2464-2470.

Zhang, H., Davison, W., Gadi, R. & Kobayashi, T. (1998), In situ measurement of dissolved phosphorus in natural waters using DGT. *Analytica Chimica Acta,* 370**,** 29-38.

9 APPENDIX

Detailed drawings for the SCAWS and its parts




A (1 : 1)
75,00° ± 0,10°
2,80 ± 0,10
52,20 ± 0,10
53,00 ± 0,10
A
Ø100,00 ± 0,10
40,20 ± 0,10
65,00 ± 0,10
Ø120,00 ± 0,10
10,00 ± 0,10
10,00 ± 0,10
118,00 ± 0,10
Designed by
thgritz
Checked by
Approved by
Date
Date
17/07/2008
Edition
Sheet
3/6
first osmo pump-1

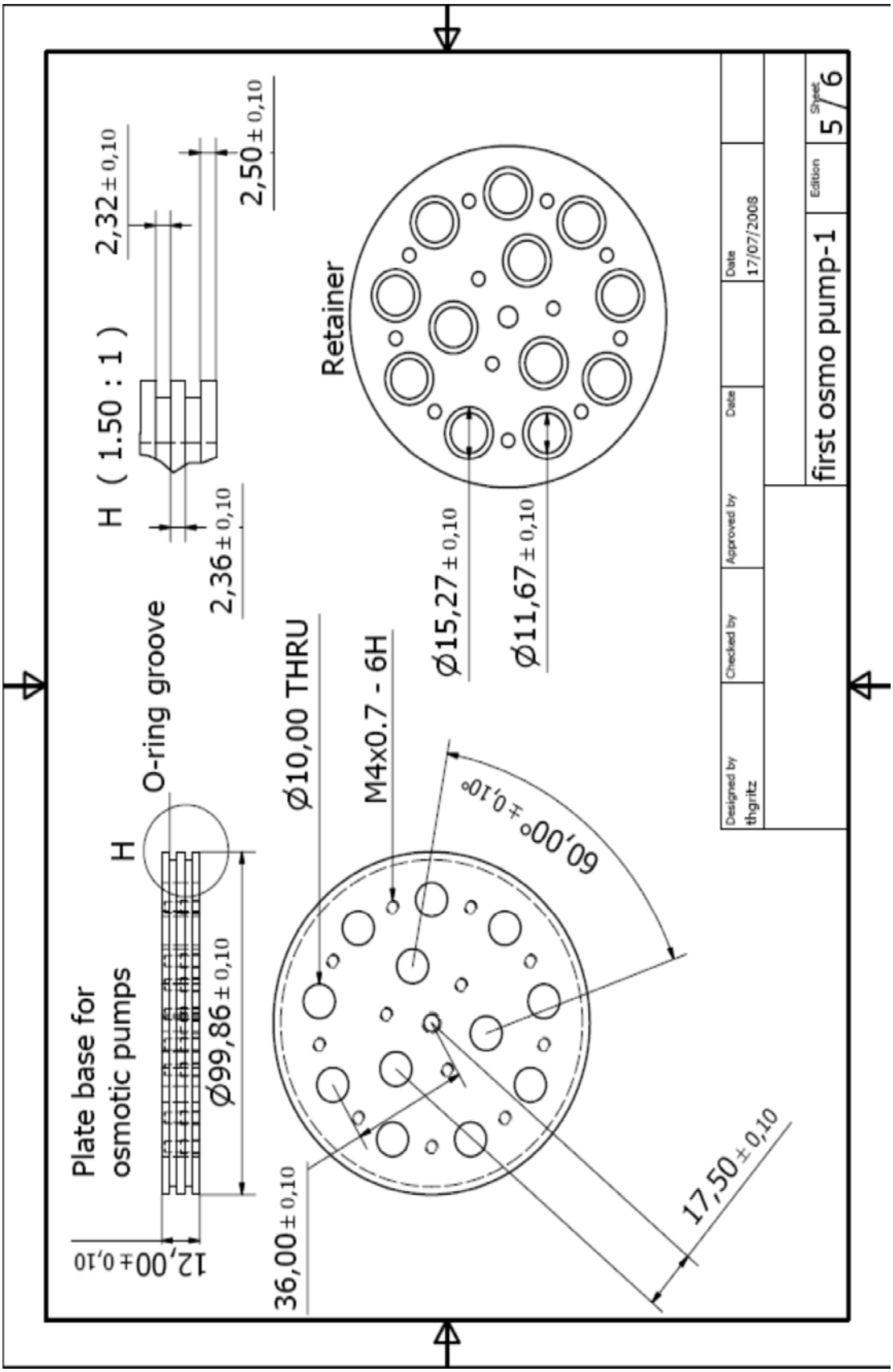
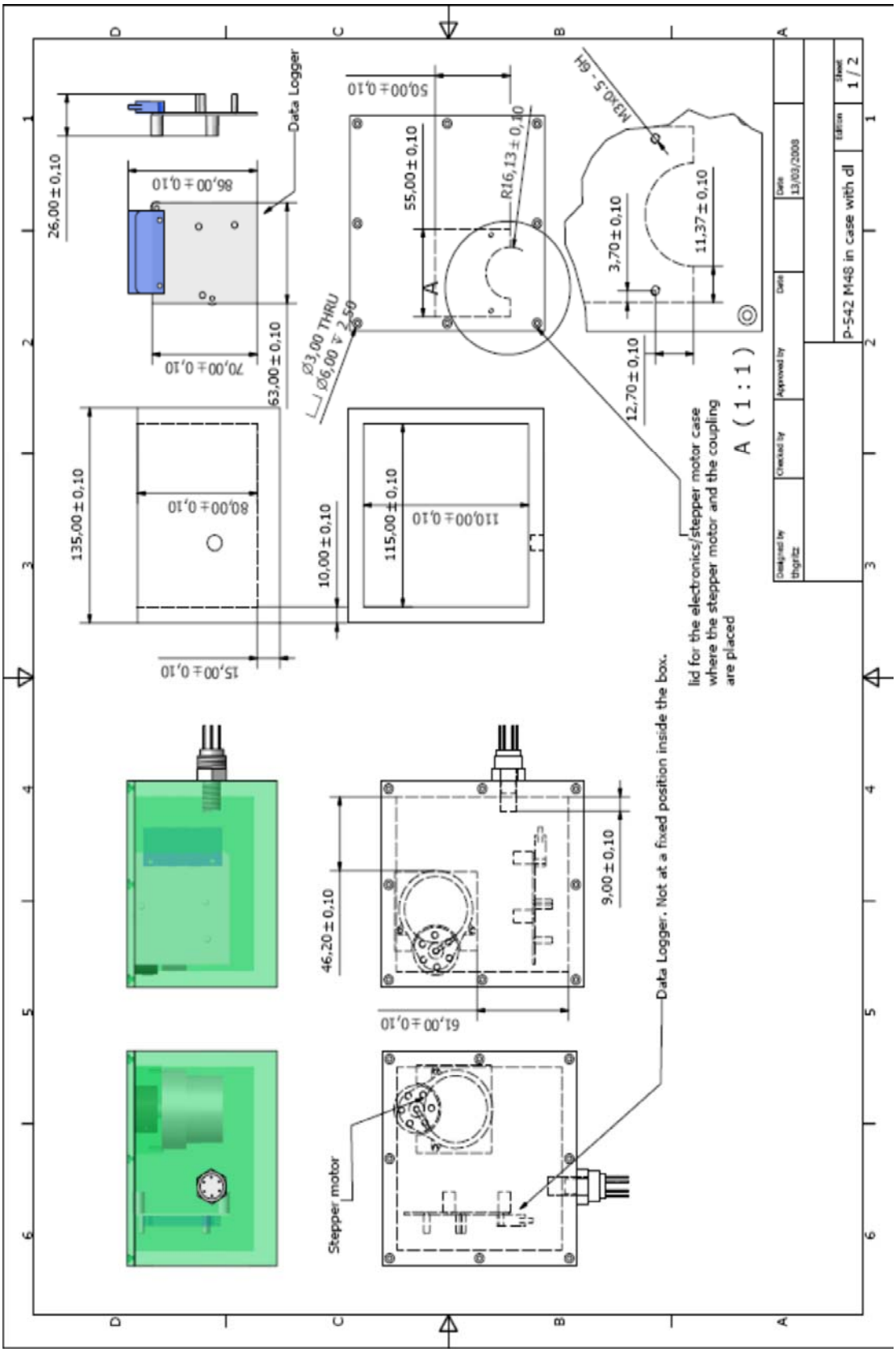
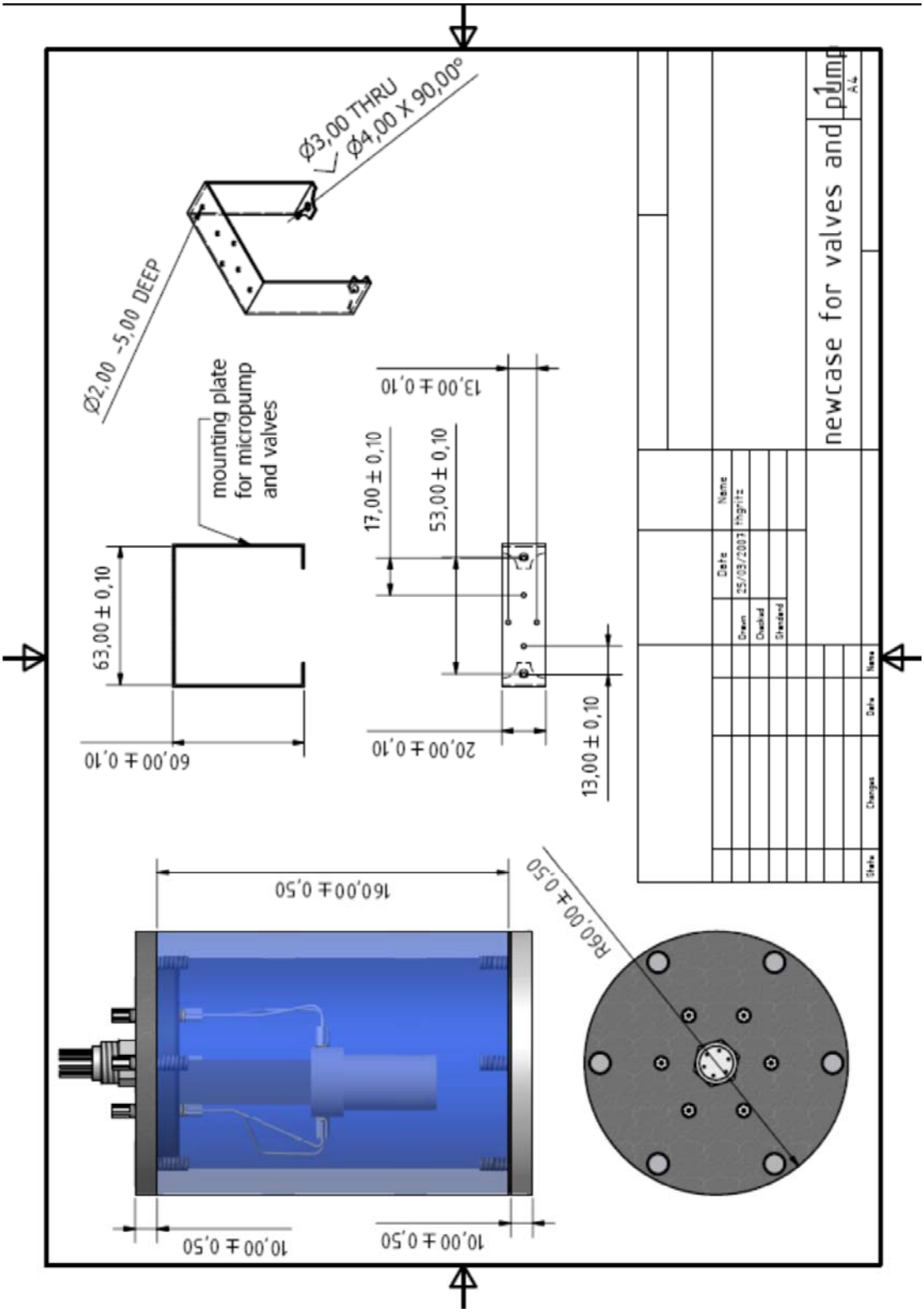
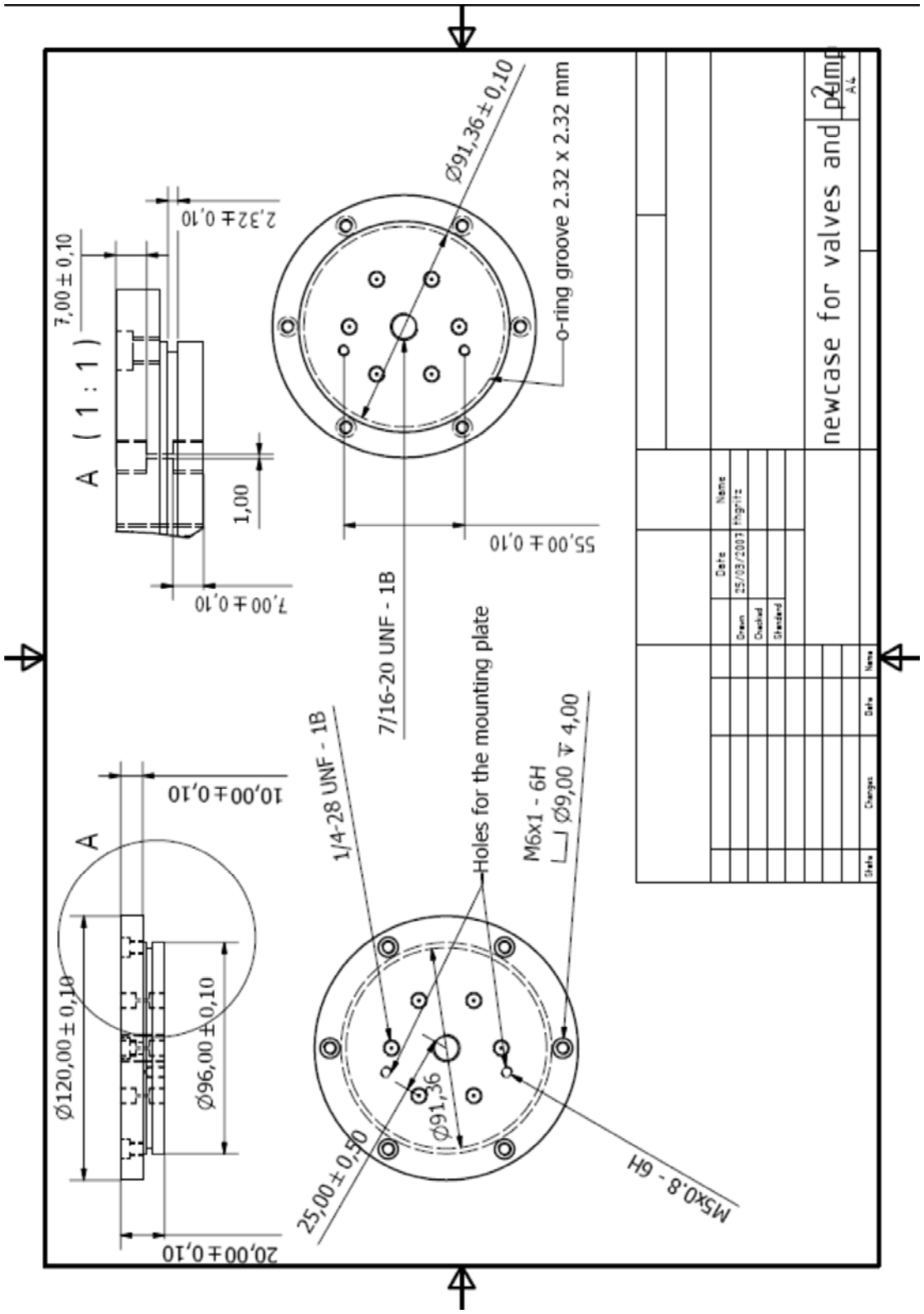
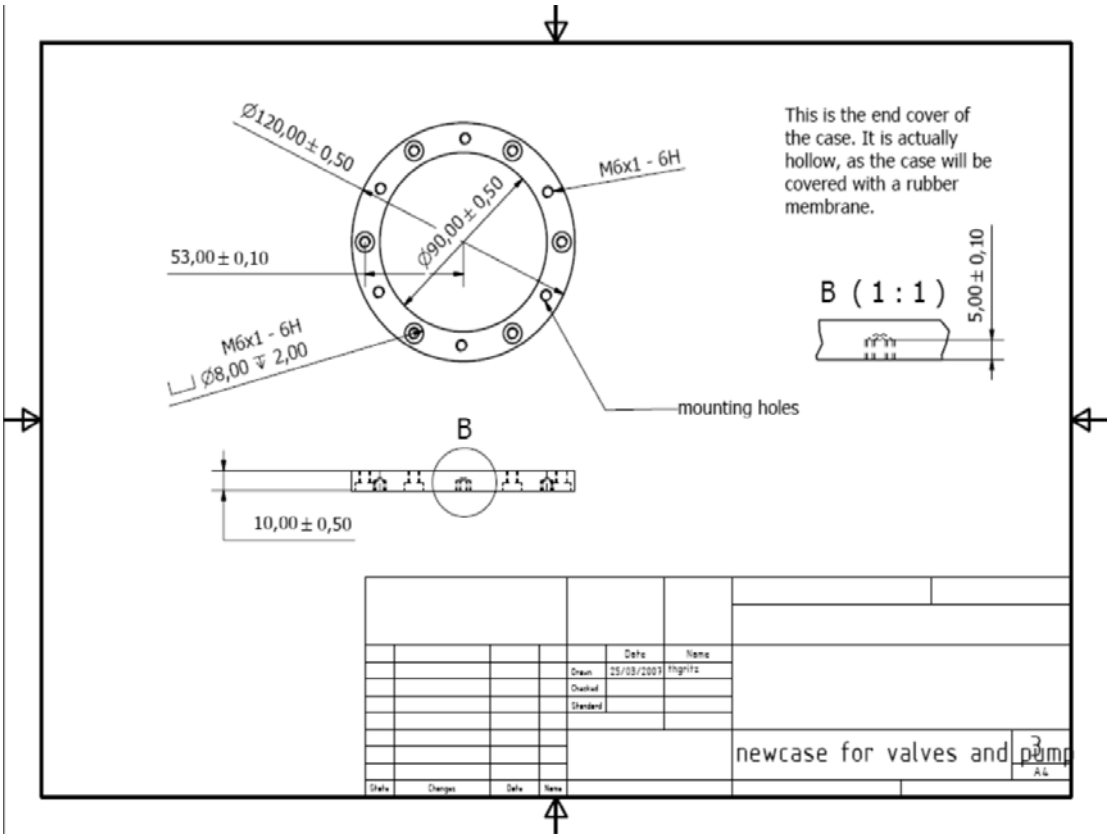


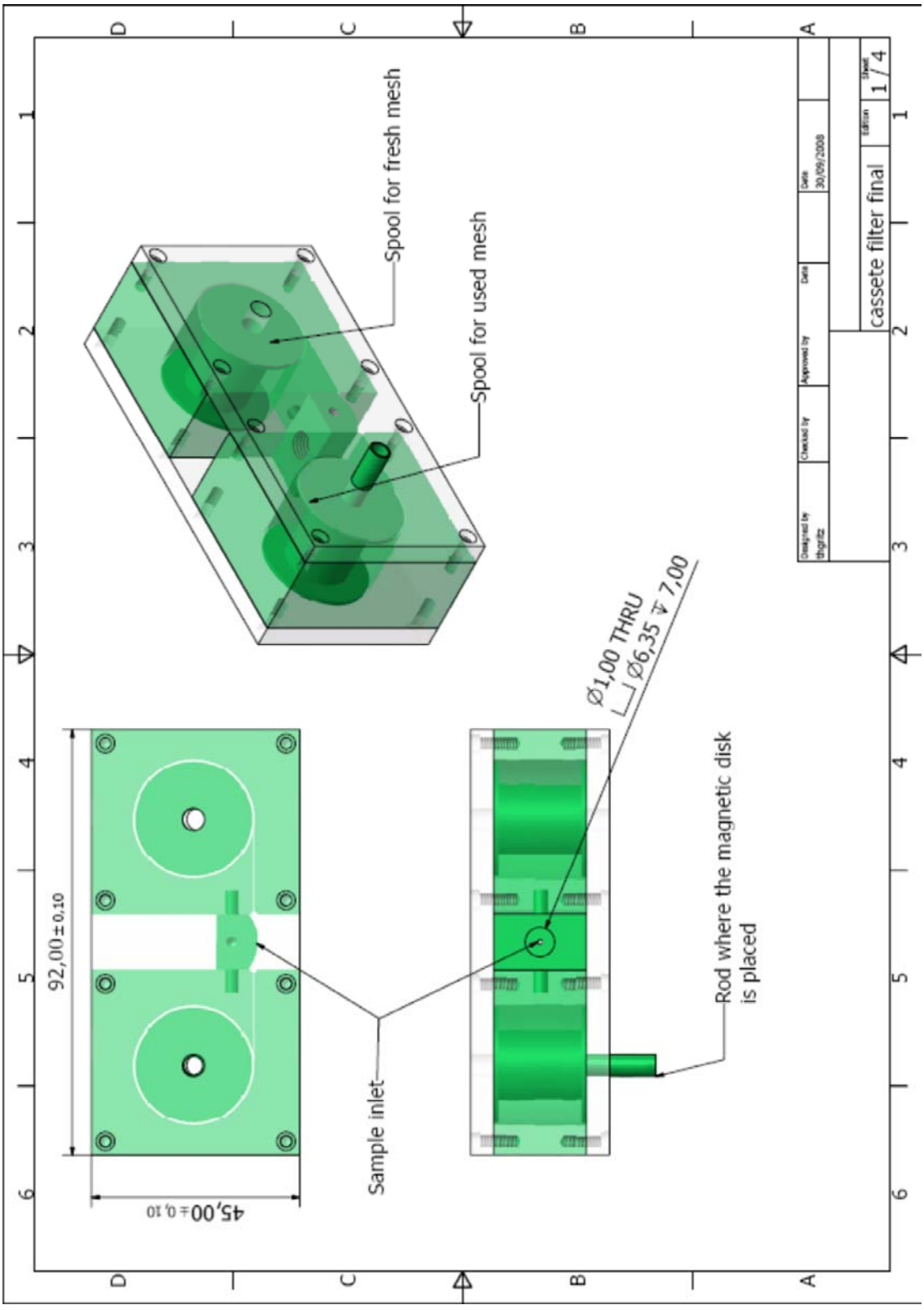
Plate base for
osmotic pumps
H
O-ring groove
12,00 ± 0,10
Ø99,86 ± 0,10
36,00 ± 0,10
Ø10,00 THRU
M4x0.7 - 6H
60,00° ± 0,10°
17,50 ± 0,10
Retainer
Ø15,27 ± 0,10
Ø11,67 ± 0,10
H (1.50 : 1)
2,32 ± 0,10
2,50 ± 0,10
2,36 ± 0,10
Designed by
thgritz
Checked by
Approved by
Date
Date
17/07/2008
first osmo pump-1
Edition
Sheet
5/6

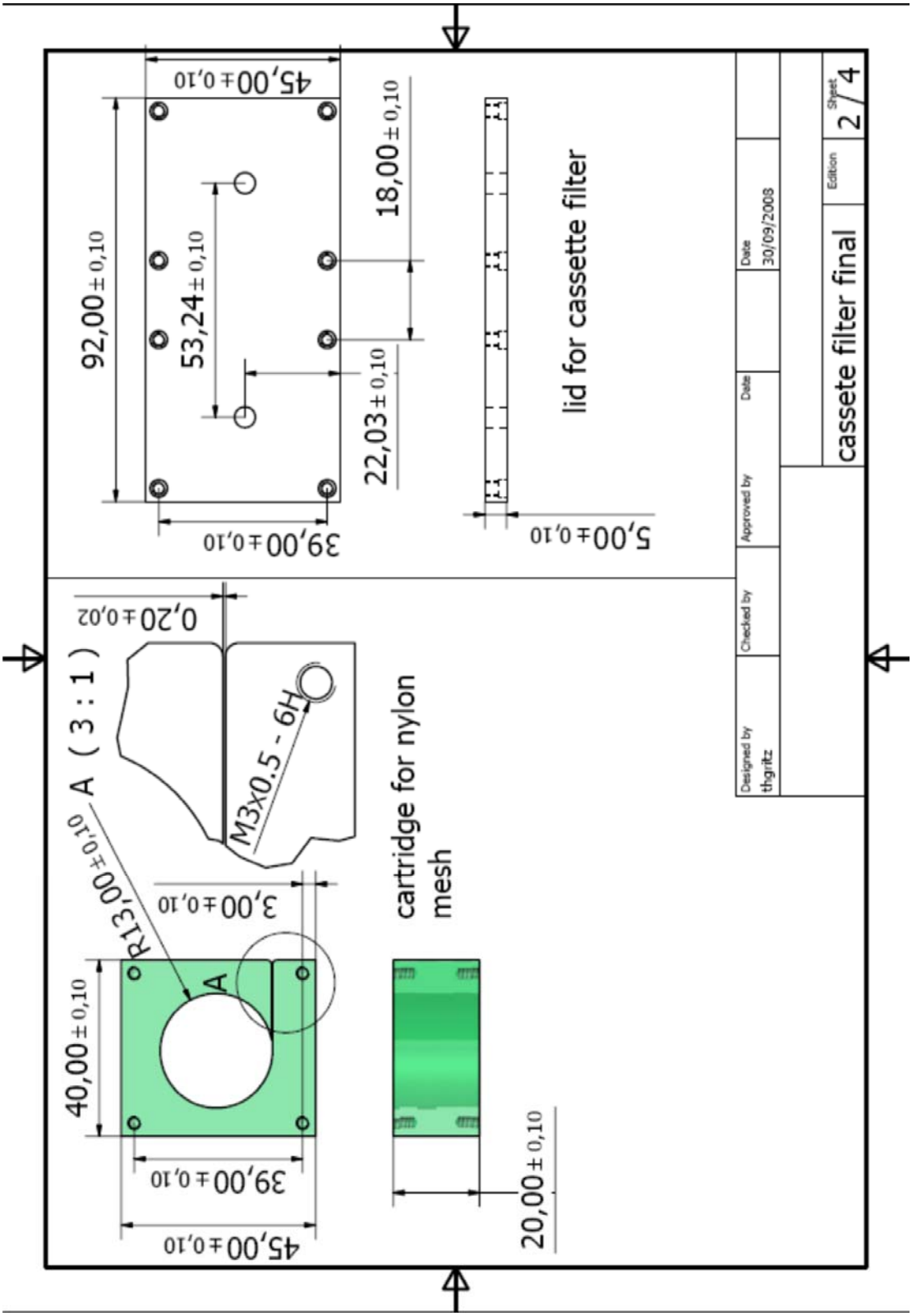

Data Logger
26,00 ± 0,10
86,00 ± 0,10
70,00 ± 0,10
63,00 ± 0,10
50,00 ± 0,10
55,00 ± 0,10
R16,13 ± 0,10
M3X0.5 - 6H
3,70 ± 0,10
11,37 ± 0,10
12,70 ± 0,10
Ø3,00 THRU
Ø6,00 x 2,50
A (1 : 1)
135,00 ± 0,10
80,00 ± 0,10
15,00 ± 0,10
10,00 ± 0,10
115,00 ± 0,10
110,00 ± 0,10
lid for the electronics/stepper motor case
where the stepper motor and the coupling
are placed
46,20 ± 0,10
9,00 ± 0,10
61,00 ± 0,10
Data Logger. Not at a fixed position inside the box.
Stepper motor
P-542 M48 in case with dl
Sheet 1 / 2
Edition
Date 13/03/2008
Approved by
Checked by
Designed by thgritz

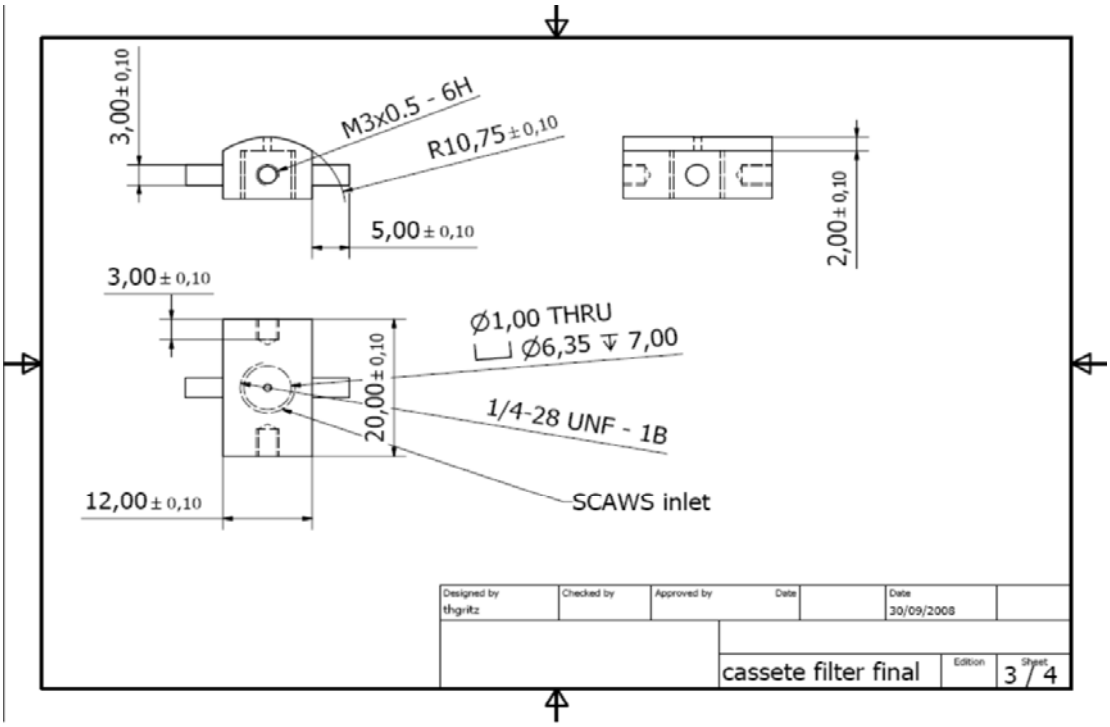

Ø3,00 THRU
Ø4,00 X 90,00°
Ø2,00 -5,00 DEEP
mounting plate
for micropump
and valves
63,00 ± 0,10
60,00 ± 0,10
13,00 ± 0,10
17,00 ± 0,10
53,00 ± 0,10
20,00 ± 0,10
13,00 ± 0,10
160,00 ± 0,50
R60,00 ± 0,50
10,00 ± 0,50
10,00 ± 0,50
newcase for valves and pump
A4
Name
Date
Drawn
Checked
Standard
Changes
Date
Name

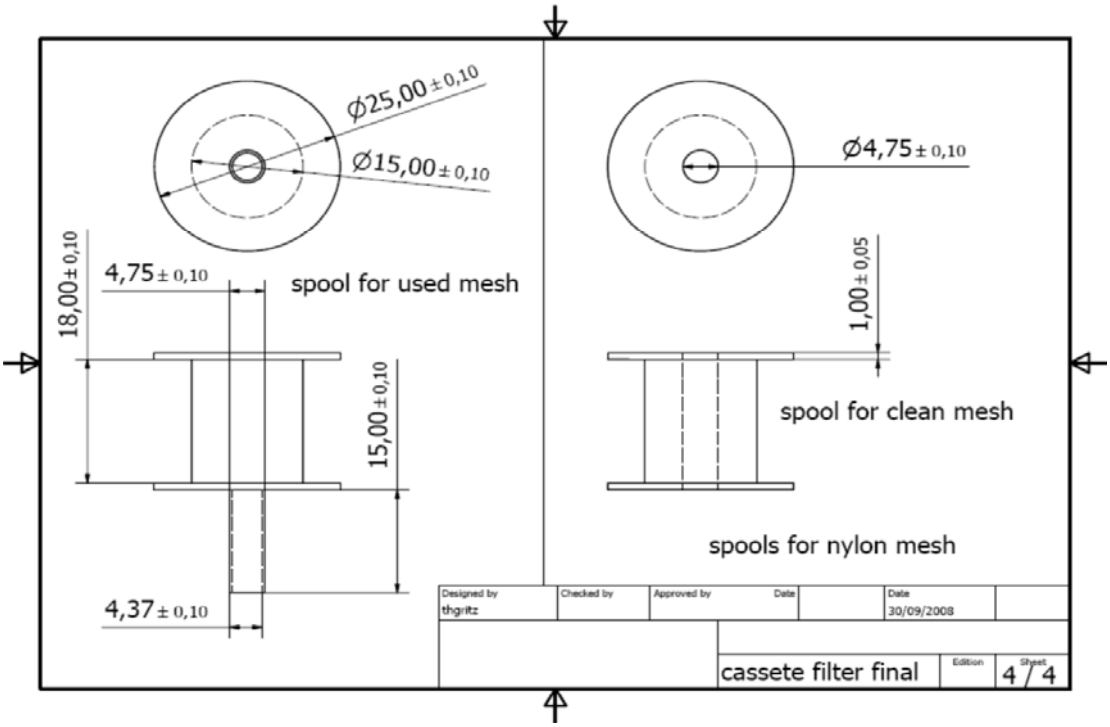

newcase for valves and pump
Ø91,36±0,10
o-ring groove 2.32 x 2.32 mm
55,00 ± 0,10
7/16-20 UNF - 1B
1/4-28 UNF - 1B
Holes for the mounting plate
M6x1 - 6H
⌴ Ø9,00 ↧ 4,00
Ø91,36
25,00±0,50
M5X0.8 - 6H
A (1 : 1)
2,32± 0,10
7,00 ± 0,10
1,00
7,00 ± 0,10
A
10,00± 0,10
Ø120,00 ± 0,10
Ø96,00 ± 0,10
20,00± 0,10


Ø120,00 ± 0,50
M6x1 - 6H
Ø90,00 ± 0,50
53,00 ± 0,10
M6x1 - 6H
⌴ Ø8,00 ↧ 2,00
mounting holes
This is the end cover of the case. It is actually hollow, as the case will be covered with a rubber membrane.
B (1 : 1)
5,00 ± 0,10
B
10,00 ± 0,50
Date
Name
Drawn
25/03/2007
thgnitz
Checked
Standard
newcase for valves and pump
3
A4
Sheets
Changes
Date
Name


Spool for fresh mesh
Spool for used mesh
Ø1,00 THRU
⌴ Ø6,35 ↧ 7,00
Rod where the magnetic disk is placed
Sample inlet
92,00 ± 0,10
45,00 ± 0,10
cassete filter final
Sheet 1 / 4
Date 30/09/2008
Drawing by dhgiritz

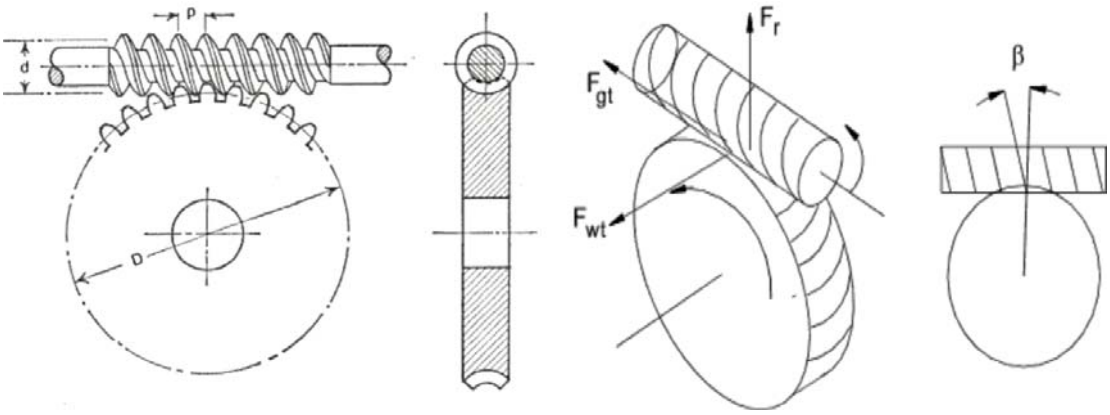

45,00 ± 0,10
92,00 ± 0,10
53,24 ± 0,10
18,00 ± 0,10
22,03 ± 0,10
39,00 ± 0,10
lid for cassette filter
5,00 ± 0,10
0,20 ± 0,02
A (3 : 1)
M3x0,5 - 6H
R13,00 ± 0,10
A
3,00 ± 0,10
cartridge for nylon
mesh
40,00 ± 0,10
39,00 ± 0,10
45,00 ± 0,10
20,00 ± 0,10
Designed by
thgritz
Checked by
Approved by
Date
Date
30/09/2008
Edition
Sheet
2/4
cassete filter final


3,00 ± 0,10
M3x0.5 - 6H
R10,75 ± 0,10
5,00 ± 0,10
2,00 ± 0,10
3,00 ± 0,10
Ø1,00 THRU
⌴ Ø6,35 ↧ 7,00
20,00 ± 0,10
1/4-28 UNF - 1B
12,00 ± 0,10
SCAWS inlet
Designed by
thgritz
Checked by
Approved by
Date
Date
30/09/2008
cassete filter final
Edition
Sheet
3 / 4


Ø25,00 ± 0,10
Ø15,00 ± 0,10
Ø4,75 ± 0,10
18,00 ± 0,10
4,75 ± 0,10
spool for used mesh
1,00 ± 0,05
15,00 ± 0,10
spool for clean mesh
spools for nylon mesh
4,37 ± 0,10
Designed by
thgritz
Checked by
Approved by
Date
Date
30/09/2008
cassete filter final
Edition
Sheet
4 / 4

Calculation of torque for worm – gear mechanism

The forces that are applied on the system are presented in the following diagram (http://www.roymech.co.uk/Useful_Tables/Drive/Worm_Gears.html).



Where:

d = worm pitch diameter

p= pitch for worm and wheel

D = wheel/gear pitch diameter

The relationship between the output torque M_2 and the input torque M_1 is described by the following equation:

$$M_2 = \left(M_1 \cdot \frac{d_2}{d_1}\right) \cdot \left[\frac{(cosa_n - \mu \cdot tan\gamma)}{(cosa_n \cdot tan\gamma + \mu)}\right]$$

Where:

M_1 = Input torque. We assume that it is the torque of the stepper motor (35 gcm = 0.0034 Nm)

M_2 = Output torque (Nm)

d_1 = Reference diameter of worm 0.00953 m

d_2 = Reference diameter of wheel/gear 0.0254 m

α_n = Normal pressure angle (20^0 = 0.349 rads)

μ = friction coefficient for Delrin (0.073, value obtained from HPC Gears Ltd.)

γ = worm lead angle = 0.165 rads

Substituting the above values M_2 = 0.037 Nm

Code for stepper motor and filter (C language)

```
/*********************************************************************/
// Data logger code for Thanos's filter project v2.0 24-07-2007       //
// main function and interrupt servicing                              //
//Low power uses approx 450 uA in sleep mode                          //
/*********************************************************************/
#include "data_logger_v1-1.h"
#include "DS1339_rtc.c"              // Realtime clock
#include "thanos_filter.c"
#include "filter_go_sleep.c"
#byte myintcon = 0x4051
// Project specific functions

//#use delay(clock=10000000)            // uses a 10Mhz Xtal

void go_sleep();
int alarm_count;
unsigned int8 status;
int DaysRunning;                    // no of days since switch on
int16 Days_to_run;

int myintcon2;

void main()
{
  struct time_date current;
  disable_interrupts(global);// Disable interrupts till we have finished setup
  // output_high(eccp4);               //Turn on high current supply
  output_high(LED0);                // Both LEDs are lit for startup
  //output_high(LED1);                // MMC LED
  output_low(LED2);
  output_low(LED3);
  output_low(Step_OE);                // disable stepper motor
  setup_timer_0(RTCC_OFF);            // Start the timers
  setup_timer_1(T1_DISABLED);   // Slowest possible Timer1 for debugging timing
setup_timer_2(T2_DISABLED, 230, 6);  // 200Hz interrupt divided lower in isr
  setup_ccp1(CCP_OFF);
  setup_ccp2(CCP_OFF);
```

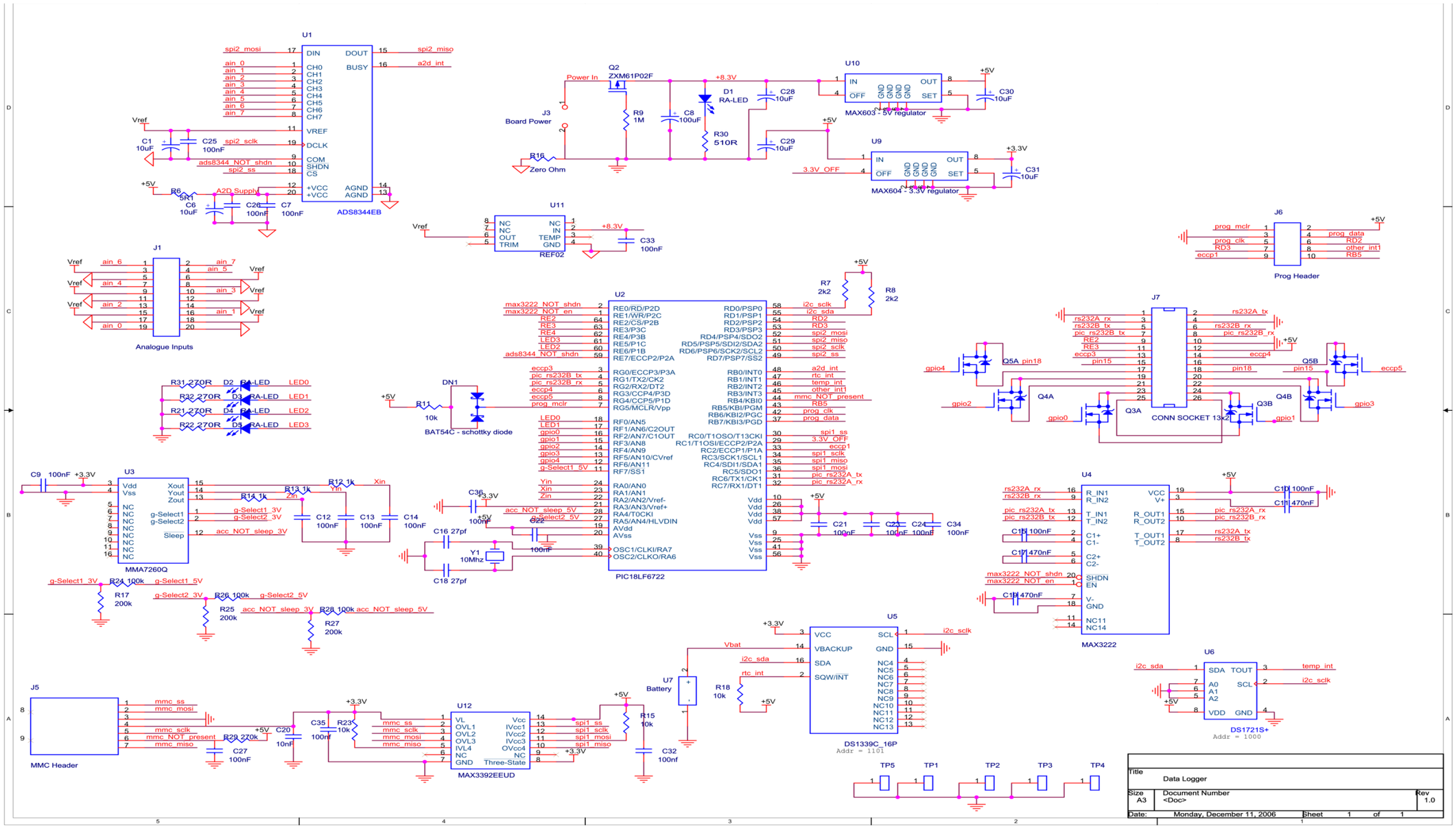
```
setup_ccp3(CCP_OFF);
setup_ccp4(CCP_OFF);
setup_ccp5(CCP_OFF);

output_low(pump);              //disable the two used ports
output_high(PumpPower);
ENABLE_3_3V;                   // Enable 3.3V
output_high(MAX3222_NSHDN);    // Enable the RS232 interface
output_low(MAX3222_NEN);
delay_ms(3);                   // Interface takes a while to become active

//ds1339_gui_set_time();       // used to initalise logger time needs RS232
Days_to_run = 365;

fprintf(rda2_strm, "\r\r\r\r\nData Logger\r\r\n");
ds1339_init();
ds1339_read_time(&current);
delay_ms(1);
fprintf(rda2_strm, "%02U:%02u   %02u:%02u:%02u\r\n",
 current.ui8_date,current.ui8_mth,current.ui8_hr,
 current.ui8_min, current.ui8_sec);
// We want to read the current time and then set an alarm

// ds1339_inc_day(&current);          //Increment by Day
//ds1339_inc_hour(&current);          //Increment by hour
ds1339_inc_minute (&current);        //Increment by Minute
ds1339_set_alarm1(&current);
//ds1339_set_alarm2(&current);       // Not currently used

 ds1339_status();                    // Reset any pending alarms

// Sort out the interrupts
clear_interrupt(int_ext1);//It is worth doing this after setting up the RTC
ext_int_edge(1, H_TO_L);
enable_interrupts(int_ext1);         // Interrupt from RTC
enable_interrupts(global);           // Setup is over

alarm_count = read_eeprom(0);        //Stored AlarmCount
fprintf(rda2_strm,"Alarm count %d\r\n",alarm_count);
```

```
  filter_pump();                        // operates pump on alarm

  if (alarm_count == 3)
    {
    fprintf(rda2_strm, "\rFunction 2     ***  Stepper  ***\r");
    filter_step();
    delay_ms(100);
    alarm_count = 0;                    // stepper motor runs every 3 alarms
    }

  alarm_count++;
  write_eeprom(0,alarm_count);

  DaysRunning= read_eeprom(1);
  fprintf(rda2_strm,"\r\ndays run %d\r\n",DaysRunning);
  DaysRunning++;
  write_eeprom(1,DaysRunning);          // stores the number
  if (DaysRunning > Days_to_run)        // Determines end of test
  {
  fprintf(rda2_strm,"\r\nclosedown\r\n");
  disable_interrupts(global);
  alarm_count = 0;
  write_eeprom(0,alarm_count);
  DaysRunning = 0;
  write_eeprom(1,DaysRunning);
  }
 output_low(LED0);
// output_low(eccp4);                   //Turn off high current supply
myintcon2 = myintcon;
fprintf(rda2_strm,"\r\nIntcon value is %d\r\n",myintcon2);
 go_sleep();
  While(1)                              //stops program ending
  {
  //output_high(LED1);                  // flashes led
 // Output_High(Power12);
 // delay_ms(5000);
 // output_low(LED1);
 // output_low(Power12);
 // delay_ms(5000);
```

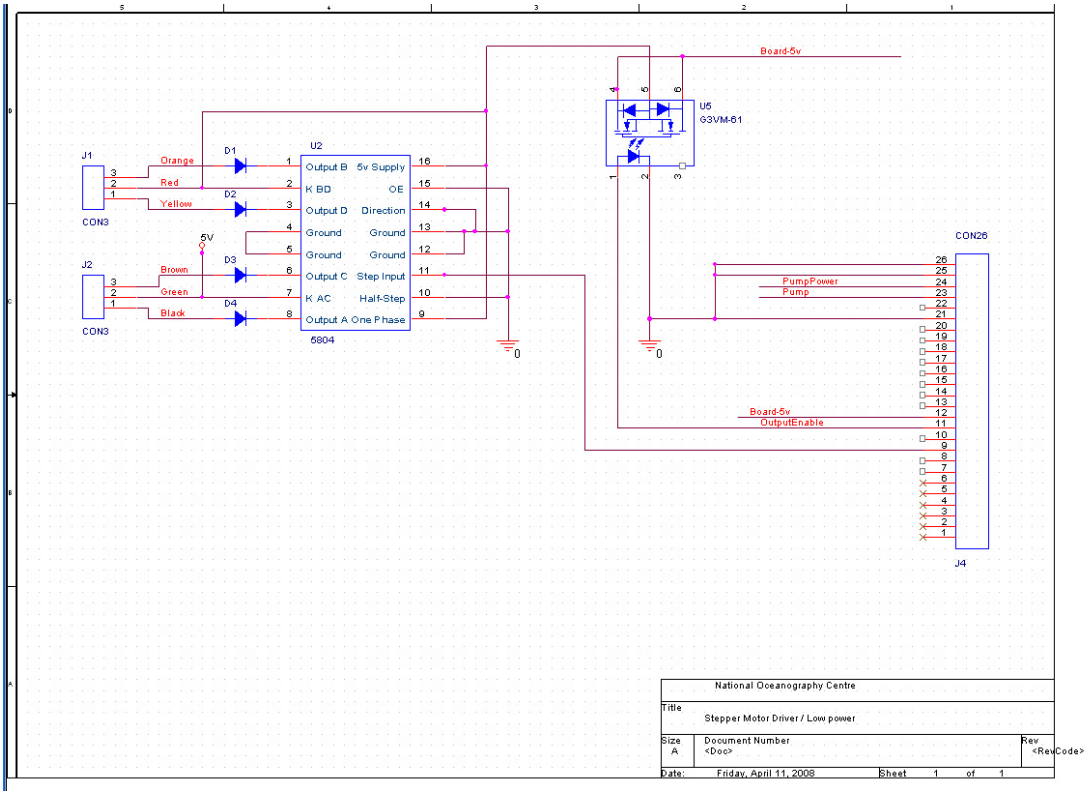
```
  }
} // end of main
#int_ext1                          // interrupt no 1
void isr_rtc_alarm()                    // The RTC is telling us to stop
{
 //  int steps;
  unsigned int8 status;
  unsigned int8 day;
  struct time_date current;
  output_high(eccp4);                   //Turn on high current supply
  output_high(pin_C1);                   //3.3 v on
  //output_high(LED0 );
  //output_high(LED1);
  setup_uart(1);                        // re-enable comms
  output_high(pin_e0);
  delay_ms(100);
  status = ds1339_status();           //reads value of status then clears it
if(bit_test(status, 0))                 // this is the expected interrupt
  {
 reset_cpu();                          //main runs again
  }
else
  {
  fprintf(rda2_strm, "Alarm 1 not active\r");// interrupt other than required
  clear_interrupt(int_ext1);
  go_sleep();
  }
}                                    //End of interupt service routine
```

Electronics

Data logger electric circuit.



Stepper motor control electric circuit



Details of YSI-660 system

YSI 6600 V2 Sensor Specifications

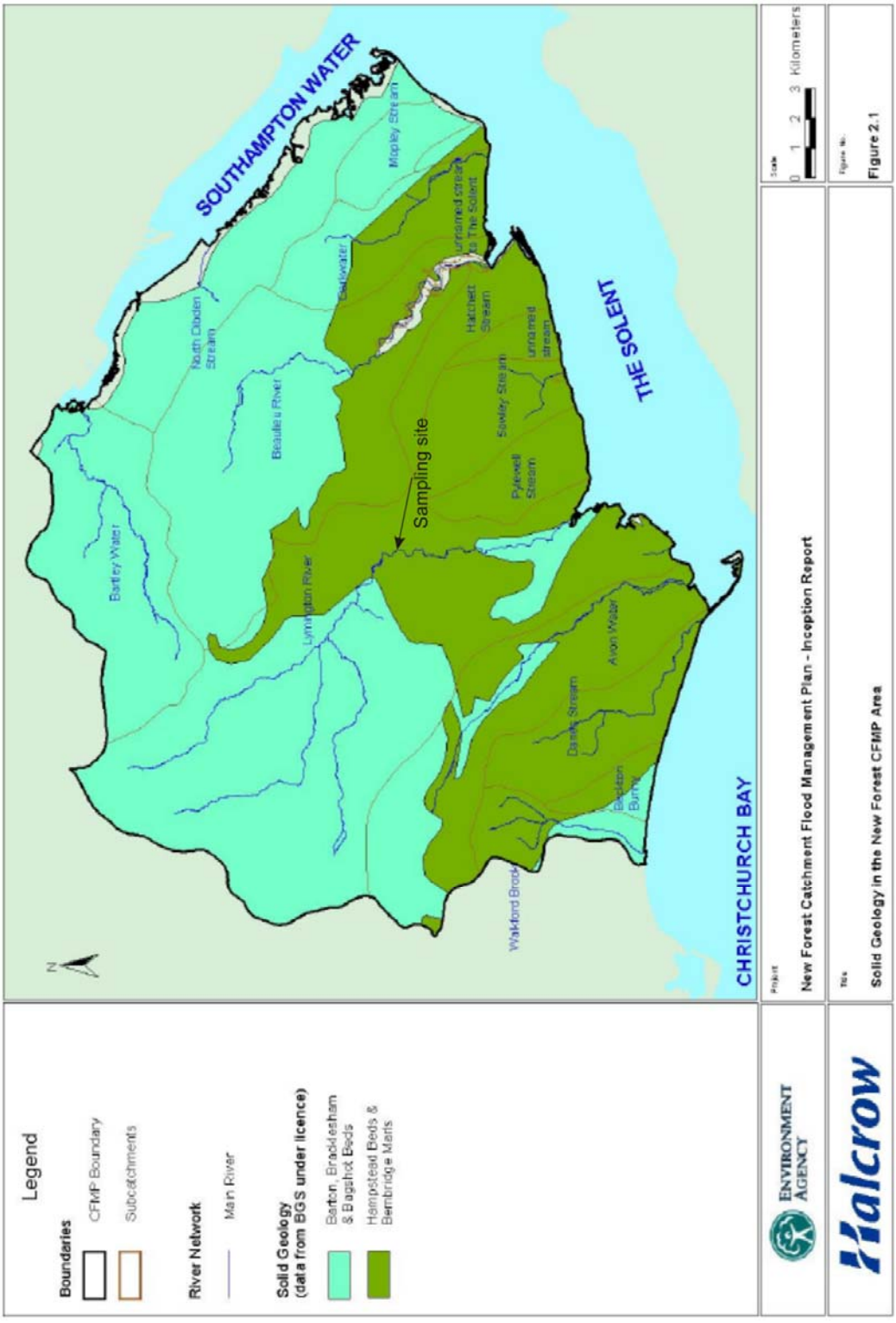
	Range	Resolution	Accuracy
ROX™ Optical Dissolved Oxygen• % Saturation	0 to 500%	0.1%	0 to 200%: ±1% of reading or 1% air saturation, whichever is greater; 200 to 500%: ±15% of reading
ROX™ Optical Dissolved Oxygen• mg/L	0 to 50 mg/L	0.01 mg/L	0 to 20 mg/L: ± 0.1 mg/L or 1% of reading, whichever is greater; 20 to 50 mg/L: ±15% of reading
Dissolved Oxygen•• % Saturation 6562 Rapid Pulse™ Sensor*	0 to 500%	0.1%	0 to 200%: ±2% of reading or 2% air saturation, whichever is greater; 200 to 500%: ±6% of reading
Dissolved Oxygen•• mg/L 6562 Rapid Pulse™ Sensor*	0 to 50 mg/L	0.01 mg/L	0 to 20 mg/L: ± 0.2 mg/L or 2% of reading, whichever is greater; 20 to 50 mg/L: ±6% of reading
Conductivity••• 6560 Sensor*	0 to 100 mS/cm	0.001 to 0.1 mS/cm (range dependent)	±0.5% of reading + 0.001 mS/cm
Salinity	0 to 70 ppt	0.01 ppt	±1% of reading or 0.1 ppt, whichever is greater
Temperature 6560 Sensor*	-5 to +50°C	0.01°C	±0.15°C
pH 6561 Sensor*	0 to 14 units	0.01 unit	±0.2 unit
ORP	-999 to +999 mV	0.1 mV	±20 mV
Depth Deep	0 to 656 ft, 200 m	0.001 ft, 0.001 m	±1 ft, ±0.3 m
Medium	0 to 200 ft, 61 m	0.001 ft, 0.001 m	±0.4 ft, ±0.12 m
Shallow	0 to 30 ft, 9.1 m	0.001 ft, 0.001 m	±0.06 ft, ±0.02 m
Vented Level	0 to 30 ft, 9.1 m	0.001 ft, 0.001 m	±0.01 ft, 0.003 m
Turbidity• 6136 Sensor*	0 to 1,000 NTU	0.1 NTU	±2% of reading or 0.3 NTU, whichever is greater**
Nitrate/nitrogen••••	0 to 200 mg/L-N	0.001 to 1 mg/L-N (range dependent)	±10% of reading or 2 mg/L, whichever is greater
Ammonium/ammonia/ nitrogen••••	0 to 200 mg/L-N	0.001 to 1 mg/L-N (range dependent)	±10% of reading or 2 mg/L, whichever is greater
Chloride••••	0 to 1000 mg/L	0.001 to 1 mg/L (range dependent)	±15% of reading or 5 mg/L, whichever is greater
Rhodamine•	0-200 µg/L	0.1 µg/L	±5% reading or 1 µg/L, whichever is greater

• Maximum depth rating for all optical probes is 200 feet, 61 m. Turbidity and Rhodamine are also available in a Deep Depth option (0 to 200 m). •• Rapid Pulse is only available on 6600 V2-2 (two optical ports version). ••• Report outputs of specific conductance (conductivity corrected to 25° C), resistivity, and total dissolved solids are also provided. These values are automatically calculated from conductivity according to algorithms found in Standard Methods for the Examination of Water and Wastewater (ed 1989). •••• Freshwater only. Maximum depth rating of 50 feet, 15.2 m. 6600 V2-2 has 3 ISE ports; not available on the 6600V2-4.				**In YSI AMCO-AEPA Polymer Standards.
	Range	Detection Limit	Resolution	Linearity
Blue-Green Algae Phycocyanin•	~0 to 280,000 cells/mL† 0 to 100 RFU	~220 cells/mL§	1 cell/mL 0.1 RFU	R2 > 0.9999**
Blue-Green Algae Phycoerythrin•	~0 to 200,000 cells/mL† 0 to 100 RFU	~450 cells/mL§§	1 cell/mL 0.1 RFU	R2 > 0.9999***
Chlorophyll• 6025 Sensor*	~0 to 400 µg/L 0 to 100 RFU	~0.1 µg/L§§§	0.1 µg/L Chl 0.1% RFU	R2 > 0.9999****
• Maximum depth rating for all optical probes is 200 feet, 61 m. Also available in a Deep Depth option (0 to 200 m). RFU = Relative Fluorescence Units	† Explanation of Ranges can be found in the 'Principles of Operation' section of the 6-Series Manual, Rev D.	§ Estimated from cultures of Microcystis aeruginosa. §§ Estimated from cultures Synechococcus sp. §§§ Determined from cultures of Isochrysis sp. and chlorophyll a concentration determined via extractions.		**For serial dilution of Rhodamine WT (0-400 ug/L). ***For serial dilution of Rhodamine WT (0-8 µg/L). ****For serial dilution of Rhodamine WT (0-500 ug/L).

YSI 6600 V2 Sonde Specifications

Medium		Fresh, sea or polluted water	Software		EcoWatch®
Temperature	Operating Storage	-5 to +50°C -10 to +60°C	Dimensions	Diameter Length, no depth Length, with depth Weight	3.5 in, 8.9 cm 19.6 in, 49.8 cm 21.6 in, 54.9 cm 7 lbs, 3.18 kg (batteries installed, with depth)
Communications		RS-232, SDI-12	Power	External Internal	12 V DC 8 C-size alkaline batteries

Geological map for New Forest – Lymington River catchment



Data from marine deployments

2nd Marine Deployment Data

Major anions and cations concentrations are in mM. Data are from the DIONEX DX500 system. Trace metals concentrations are in nM, and data are from the crICP-MS Agilent 750ce system.

SCAWS Samples	Cl	Br	NO_3	SO_4	Na	K	Mg	Ca
1	284.46	0.26	0.27	13.34	228.45	4.64	27.25	5.93
2	479.83	0.45	0.31	24.43	388.53	7.70	46.15	8.89
3	558.89	0.54	0.31	26.80	452.99	9.14	54.37	11.37
4	464.29	0.44	0.19	23.98	424.85	9.18	53.51	10.86
5	432.63	0.40	0.45	22.66	372.64	7.49	44.82	8.94

Manual Samples	Cl	Br	NO_3	SO_4	Na	K	Mg	Ca
1 (Low tide)	505.25	0.47	0.35	25.39	430.99	8.75	52.33	10.19
(High tide)	504.74	0.48	0.29	25.53	429.54	8.62	51.74	9.91
2 (Low tide)	443.84	0.41	1.05	22.23	373.28	7.48	45.34	9.10
(High tide)	478.03	0.45	0.30	24.04	397.95	7.84	48.15	9.77
3 (Low tide)	492.58	0.45	0.52	24.76	409.68	8.22	50.13	10.41
(High tide)	492.53	0.46	0.26	24.76	409.31	8.19	49.94	9.93
4 (Low tide)	476.74	0.45	0.36	23.81	397.08	8.07	48.08	9.41
(High tide)	500.31	0.46	0.33	25.17	413.87	8.29	50.57	9.76
5 (Low tide)	473.45	0.44	0.33	23.74	388.69	7.89	47.50	9.18

Average manual samples	Cl	Br	NO_3	SO_4	Na	K	Mg	Ca
1	504.99	0.47	0.32	25.46	430.26	8.69	52.03	10.05
2	460.93	0.43	0.68	23.13	385.62	7.66	46.75	9.44
3	492.55	0.46	0.39	24.76	409.49	8.20	50.03	10.17
4	488.53	0.46	0.34	24.49	405.47	8.18	49.32	9.58
5	473.45	0.44	0.33	23.74	388.69	7.89	47.50	9.18

SCAWS Samples	Mn	Ni	Cu	Zn	As	Cd	U
1	89.93	86.53	26.19	0.58	3.2	2.31	7.35
2	84.29	28.4	16.51	0.24	1.26	1.73	10.87
3	147.53	37.97	133.9	0.24	NaN	1.18	12.24
4	166.25	37.6	59.37	0.48	16.18	2.3	10.19
5	126.87	43.93	28.17	0.16	7.71	4.05	9.63

Manual Samples	Mn	Ni	Cu	Zn	As	Cd	U
1 (Low tide)	82.25	37.67	29.00	450.61	14.93	0.66	13.19
(High tide)	59.82	37.17	12.74	106.39	10.09	0.05	12.05
2 (Low tide)	132.58	73.27	31.29	826.67	9.84	2.33	10.24
(High tide)	114.51	42.37	12.17	78.42	13.69	0.60	11.38
3 (Low tide)	114.87	33.67	29.93	34.39	12.05	1.78	12.10
(High tide)	59.24	38.83	7.79	-22.57	1.48	0.63	11.55
4 (Low tide)	139.35	46.53	53.02	129.88	10.26	0.07	10.71
(High tide)	83.64	60.20	42.03	141.91	14.25	2.34	10.47
5 (Low tide)	98.84	54.53	41.65	297.82	-0.59	0.62	10.72

Average manual samples	Mn	Ni	Cu	Zn	As	Cd	U
1	71.04	37.42	20.87	0.28	12.51	0.36	12.62
2	123.55	57.82	21.73	0.45	11.77	1.47	10.81
3	87.05	36.25	18.86	NaN	6.77	1.2	11.83
4	111.49	53.37	47.52	0.14	12.25	1.21	10.59
5	98.84	54.53	41.65	0.3	NaN	0.62	10.72

3rd Marine Deployment data

SCAWS Samples	F	Cl	Br	NO_3	SO_4	Na	K	Mg	Ca
os1	0.02	473.52	0.45	35.15	21.22	418.43	10.04	43.27	12.58
os2	0.02	454.66	0.44	18.48	20.77	371.67	8.74	38.60	10.19
os3	0.02	480.41	0.46	11.91	23.56	401.51	9.74	41.98	10.97
os4	0.04	509.20	0.48	20.27	25.61	414.78	10.03	42.98	11.78
os5	0.02	468.97	0.45	15.24	21.49	399.28	9.56	42.00	11.83
os6	0.06	530.22	0.51	17.23	24.74	436.90	10.23	46.01	12.60
os7	0.05	510.02	0.49	14.75	23.25	412.51	11.71	43.42	10.64
os8	0.03	447.27	0.42	19.06	20.26	365.14	9.46	38.40	8.88
os9	0.02	482.90	0.46	17.02	21.98	384.45	9.17	39.61	9.62
os10	0.00	563.24	0.54	19.89	26.02	438.22	11.31	49.12	12.10
os11	0.00	511.80	0.49	27.81	24.04	425.41	10.00	46.16	11.69
os12	0.04	492.76	0.47	21.35	22.34	401.05	10.03	43.72	9.95

Manual Samples	F	Cl	Br	NO_3	SO_4	Na	K	Mg	Ca
1	0.02	466.02	0.45	31.74	21.43	345.60	10.28	38.61	13.65
2	0.02	479.95	0.46	35.00	22.04	386.50	11.01	43.33	14.10
3	0.03	439.45	0.41	27.52	21.73	352.54	9.39	39.19	12.28
4	0.06	508.44	0.48	12.57	23.46	317.42	9.26	36.18	10.03
5	0.03	483.57	0.46	26.39	22.24	380.59	9.72	41.15	12.41
6	0.06	503.56	0.48	22.09	23.24	391.28	9.87	43.13	13.72
7	0.08	517.83	0.50	23.93	23.80	399.46	10.69	44.63	11.87
8	0.00	511.90	0.49	19.36	23.57	400.12	10.11	43.83	13.02
9	0.03	441.38	0.42	26.87	23.26	392.35	9.53	43.23	13.15
10	0.05	522.33	0.50	19.86	24.05	395.29	9.85	42.71	12.58
11	0.03	483.92	0.46	26.93	22.20	385.90	10.17	42.65	12.36
12	0.04	406.50	0.39	31.21	21.59	367.10	9.61	40.41	10.17

SCAWS Samples	Mn	Ni	Cu	Zn	As	Cd	U
1	127.19	53.67	131.78	1.96	33.90	0.71	11.20
2	116.58	52.10	168.73	0.46	31.12	1.42	10.60
3	102.31	46.92	238.47	0.59	24.36	0.71	10.99
4	106.98	70.59	186.83	1.48	36.26	2.15	10.86
5	87.82	39.37	221.14	0.79	21.90	2.88	10.60
6	77.93	27.64	52.44	0.36	23.62	2.00	11.69
7	103.26	17.41	133.92	0.57	41.79	2.11	10.51
8	96.63	4.03	26.64	0.37	11.60	2.14	9.18
9	92.76	50.90	54.26	0.31	54.33	9.63	11.39
10	84.23	1.40	51.16	0.42	29.27	0.72	11.65
11	70.48	-17.17	-11.88	0.33	28.84	1.38	10.91
12	24.28	-0.82	30.77	0.43	9.06	2.11	10.77

Manual Samples	Mn	Ni	Cu	Zn	As	Cd	U
1	165.51	42.93	72.39	0.44	48.72	2.10	10.51
2	153.53	35.83	151.31	0.42	16.81	0.70	11.59
3	149.44	28.73	74.43	0.96	38.28	0.70	9.70
4	108.45	1.74	5.45	0.59	26.34	0.71	11.40
5	136.46	-18.07	12.35	0.35	28.77	0.00	9.80
6	148.15	-15.21	-14.17	0.38	26.04	1.38	10.05
7	145.86	-46.60	-27.42	0.31	37.96	1.38	10.32
8	122.87	-37.80	17.34	0.26	25.97	0.69	10.88
9	122.01	-24.17	36.44	0.52	28.71	1.42	10.86
10	121.95	-42.23	37.04	0.37	26.29	1.42	10.37
11	125.49	-52.07	-33.90	0.46	13.37	0.69	9.92
12	162.29	-35.29	10.70	0.30	30.65	1.38	9.64

Data from River deployments

1st Test Deployment

Major anions and cations concentrations are in mM. Data are from the DIONEX DX500 system. Trace metals concentrations are in nM, and data are from the crICP-MS Agilent 750ce system.

SCAWS Samples	Cl	SO4	NO3	HCO_3	Na	K	Mg	Ca
1	0.885	0.156	0.040	As manual samples	0.835	0.028	0.076	0.195
2	0.900	0.157	0.047		0.710	0.055	0.137	0.326
3	0.887	0.173	0.042		0.704	0.053	0.138	0.334
4	0.755	0.156	0.055		0.788	0.055	0.153	0.365
5	0.789	0.158	0.039		0.695	0.059	0.138	0.339
6	0.769	0.158	0.048		0.709	0.059	0.144	0.350
7	0.868	0.162	0.053		0.708	0.056	0.142	0.334

Manual Samples	Cl	SO4	NO3	HCO_3	Na	K	Mg	Ca
1	0.796	0.173	0.047	0.375	0.693	0.054	0.139	0.323
2	0.715	0.154	0.034	0.375	0.641	0.047	0.127	0.282
3	0.773	0.172	0.050	0.401	0.681	0.051	0.134	0.310
4	NaN	NaN	NaN	NaN	NaN	NaN	NaN	NaN
5	0.785	0.170	0.040	0.401	0.683	0.053	0.137	0.319
6	0.753	0.150	0.034	0.376	0.649	0.048	0.130	0.285
7	0.749	0.133	0.038	0.3256	0.642	0.046	0.121	0.275

SCAWS samples	Mn	Fe	Ni	Cu	Zn	Cd	U
1	1.03	4.38	0.11	0.21	2.29	9.78	1.89
2	1.74	1.82	0.10	0.09	1.25	8.47	1.83
3	2.11	7.52	0.17	6.59	6.74	8.43	2.25
4	1.81	10.07	0.15	6.52	6.97	9.34	2.10
5	3.54	7.09	0.19	6.46	6.52	9.43	2.15
6	1.63	6.88	0.17	6.54	7.24	9.86	2.09
7	1.21	6.59	0.15	6.67	6.81	9.96	2.00
Manual Samples	Mn	Fe	Ni	Cu	Zn	Cd	U
1	1.70	11.30	0.12	5.13	7.72	4.71	1.09
2	1.69	11.01	0.11	5.25	4.99	4.74	1.03
3	1.68	10.25	0.13	5.30	4.95	4.75	1.10
4	-	-	-	-	-	-	-
5	1.56	9.85	0.12	5.32	5.32	5.54	1.07
6	1.78	10.48	0.11	5.23	5.44	5.25	1.01
7	1.45	10.65	0.11	5.22	5.12	4.98	1.06

2nd River deployment (30 days)

SCAWS	Cl	SO_4	NO_3	HCO_3	Na	K	Mg	Ca
1	0.938	0.178	0.130		1.1	0.09	0.2	0.59
2	0.919	0.183	0.146		1.13	0.1	0.2	0.61
3	0.917	0.171	0.131		1.08	0.09	0.2	0.57
4	0.918	0.162	0.122		1.08	0.09	0.2	0.56
5	0.911	0.163	0.131		1.08	0.09	0.2	0.56
6	1.018	0.165	0.129		1.24	0.09	0.19	0.55
7	1.010	0.175	0.159		1.21	0.09	0.2	0.6
8	0.974	0.174	0.164		1.15	0.09	0.2	0.6
9	0.979	0.175	0.179		1.14	0.1	0.21	0.62
10	0.996	0.179	0.183		1.16	0.1	0.2	0.63
11	1.004	0.190	0.224		1.18	0.11	0.2	0.67
12	1.063	0.198	0.260		1.26	0.13	0.2	0.7
13	0.613	0.099	0.054	As manual samples	0.78	0.07	0.11	0.34
14	0.640	0.119	0.029		0.77	0.05	0.11	0.26
15	0.595	0.101	0.019		0.72	0.05	0.11	0.26
16	0.681	0.101	0.026		0.82	0.04	0.11	0.25
17	0.647	0.109	0.030		0.76	0.05	0.12	0.29
18	0.761	0.130	0.045		0.87	0.05	0.15	0.39
19	0.802	0.125	0.045		0.88	0.05	0.14	0.38
20	0.745	0.115	0.050		0.86	0.05	0.14	0.36
21	0.485	0.062	0.018		0.61	0.04	0.08	0.23
22	0.618	0.098	0.028		0.74	0.05	0.1	0.28
23	0.727	0.118	0.043		0.84	0.05	0.13	0.31
24	0.777	0.130	0.059		0.87	0.05	0.14	0.36
25	0.813	0.137	0.074		0.9	0.06	0.14	0.39
26	0.875	0.145	0.097		0.96	0.06	0.15	0.42
27	0.848	0.155	0.101		0.93	0.07	0.16	0.45
28	0.812	0.154	0.090		0.88	0.07	0.16	0.45
29	0.939	0.178	0.195		1.02	0.08	0.17	0.55
30	0.815	0.171	0.126		0.88	0.08	0.17	0.51

Manual Samples	Cl	SO_4	NO_3	HCO_3	Na	K	Mg	Ca
1	0.901	0.178	0.126	0.625	1.04	0.11	0.21	0.59
2	0.862	0.184	0.145	0.749	1.07	0.10	0.21	0.62
3	0.794	0.165	0.100	0.749	0.95	0.09	0.21	0.60
4	0.806	0.156	0.130	0.749	0.97	0.09	0.21	0.58
5	0.676	0.140	0.094	0.749	0.84	0.08	0.18	0.56
6	0.818	0.161	0.133	0.799	1.00	0.09	0.20	0.60
7	0.887	0.176	0.166	0.774	1.10	0.10	0.22	0.63
8	0.939	0.190	0.180	0.799	1.13	0.13	0.22	0.69
9	0.949	0.182	0.201	0.774	1.16	0.11	0.22	0.67
10	0.965	0.190	0.000	0.795	1.17	0.11	0.20	0.63
11	0.678	0.142	0.168	0.815	0.87	0.08	0.16	0.54
12	0.577	0.148	0.169	0.905	0.76	0.08	0.13	0.54
13	0.347	0.079	0.037	0.273	0.48	0.07	0.10	0.25
14	0.453	0.094	0.021	0.262	0.57	0.05	0.11	0.24
15	0.595	0.126	0.029	0.208	0.71	0.05	0.15	0.33
16	0.314	0.064	0.014	0.285	0.42	0.03	0.08	0.20
17	0.426	0.084	0.016	0.182	0.56	0.04	0.11	0.25
18	0.559	0.104	0.029	0.259	0.68	0.05	0.13	0.33
19	0.436	0.091	0.033	0.454	0.55	0.04	0.12	0.31
20	0.637	0.113	0.039	0.472	0.78	0.06	0.16	0.39
21	0.422	0.075	0.022	0.236	0.56	0.05	0.11	0.30
22	-	-	-	0.225	-	-	-	-
23	0.536	0.104	0.026	0.345	0.68	0.05	0.13	0.33
24	0.588	0.118	0.039	0.463	0.74	0.06	0.15	0.39
25	0.553	0.113	0.050	0.508	0.71	0.06	0.14	0.38
26	0.654	0.131	0.065	0.566	0.82	0.07	0.17	0.46
27	0.467	0.095	0.047	0.557	0.60	0.05	0.13	0.36
28	0.368	0.088	0.042	0.659	0.49	0.04	0.11	0.34
29	0.874	0.177	0.172	0.637	1.13	0.10	0.20	0.62
30	0.790	0.174	0.129	0.650	1.00	0.09	0.19	0.59

SCAWS Samples	Mn	Fe	Ni	Cu	Zn	U
1	88.26	31.32	4.59		38.61	0.04
2	59.40	50.00	3.15	6.03	26.68	0.04
3	22.13	72.77	3.09	6.15	22.97	0.05
4	13.50	97.27	3.84	6.52	27.09	0.05
5	12.84	119.20	3.93	7.63	22.36	0.04
6	10.51	157.80	4.48	8.35	34.76	0.04
7	6.23	208.10	2.91	5.80	13.73	0.06
8	8.89	295.40	3.87	7.39	25.57	0.05
9	5.11	279.90	2.16	4.03	12.41	0.05
10	6.79	254.00	1.97	4.04	10.12	0.06
11	3.64	232.50	2.66	6.59	15.50	0.06
12	2.69	202.10	2.00	3.40		0.03
13	22.62	651.50	2.55	5.57	18.63	0.06
14	36.66	158.60	3.96	8.40	40.82	0.04
15	9.89	161.40	2.16	3.67	21.09	0.05
16	18.11	217.60	2.02	5.37	13.95	0.05
17	11.30	211.00	2.06	3.12		0.05
18	4.16	220.50	2.06	4.05	11.92	0.04
19	2.17	230.10	1.70	3.24	37.53	0.04
20	2.53	223.60	2.10	3.81	23.81	0.02
21	4.90	390.90	2.93	5.06	40.05	0.07
22	18.10	258.90	2.31	3.68	23.93	0.04
23	3.57	220.00	2.70	3.85	18.15	0.03
24	2.37	239.30	1.90	4.55	16.34	0.04
25	5.34	252.40	3.36	4.55	22.02	0.02
26	3.42	269.20	2.74	3.55	21.35	0.03
27	7.63	261.10	5.12	7.53	40.02	0.03
28	23.32	350.90	3.73	2.76	9.69	0.05
29	14.47	349.50	2.78	2.49	5.74	0.05
30	21.35	542.10	12.41			0.06

Manual Samples	Mn	Fe	Ni	Cu	Zn	U
1	122.40	1175.00	3.46	1.05	2.34	0.13
2	110.20	1098.00	3.56	0.03	4.41	0.14
3	94.63	1127.00	3.96	0.08	2.09	0.13
4	85.76	1182.00	3.95	0.05	1.94	0.14
5	85.65	1185.00	2.68	0.04		0.15
6	95.42	1248.00	3.39	1.08	9.36	0.13
7	100.80	1110.00	3.51	1.39	7.11	0.15
8	105.30	1101.00	3.93	1.56	4.10	0.14
9	95.40	1177.00	3.25	0.16	3.53	0.13
10	99.37	993.20	3.21	1.36	2.69	0.13
11	102.50	1066.00	3.32	1.61	3.83	0.14
12	124.90	927.80	3.35	1.02	4.22	0.14
13	173.40	722.10	2.45	0.71	2.65	0.13
14	116.10	710.90	3.06	0.96	5.85	0.15
15	76.08	783.00	3.49	0.59	2.42	0.13
16	68.39	801.60	2.89	0.55	4.46	0.14
17	62.16	871.10	3.15	0.44	4.00	0.14
18	75.84	759.00	3.59	0.73	13.19	0.16
19	75.60	726.20	3.38	0.32	2.68	0.19
20	72.31	769.90	3.86	0.91	3.34	0.18
21	95.79	934.70	3.32	0.84	5.91	0.15
22	79.36	894.60	3.13	0.58	5.79	0.16
23	81.75	705.50	3.44	0.42	1.28	0.14
24	78.81	679.20	3.59	0.29	1.07	0.14
25	78.47	750.20	3.91	1.27	3.44	0.14
26	81.47	827.20	3.78	0.17	10.14	0.14
27	83.98	743.30	3.76	0.45	0.48	0.14
28	89.91	846.40	4.36	0.04	0.17	0.13
29	107.30	975.90	4.78	1.53	1.75	0.13
30	104.80	1026.00	6.00	1.11		0.14

Major Cations concentrations, from crICP-MS, that were used for the comparison of the two analytical methods (see section 4.4.3.4 : Comparison between crICP-MS and IC). Data are from the one month river deployment and all values are in mM.

	DIONEX DX500 - SCAWS Samples				Agilent 750ce - SCAWS Samples				
	Na	K	Mg	Ca	Na	K	Mg	^{43}Ca	^{44}Ca
1	0.88	0.08	0.17	0.51	0.97	0.13	0.18	0.50	0.48
2	1.02	0.08	0.17	0.55	1.04	0.09	0.18	0.44	0.43
3	0.88	0.07	0.16	0.45	0.93	0.08	0.18	0.39	0.37
4	0.93	0.07	0.16	0.45	1.06	0.10	0.18	0.40	0.38
5	0.96	0.06	0.15	0.42	1.17	0.10	0.19	0.36	0.34
6	0.90	0.06	0.14	0.39	1.15	0.09	0.19	0.34	0.33
7	0.87	0.05	0.14	0.36	1.08	0.08	0.17	0.29	0.28
8	0.84	0.05	0.13	0.31	1.05	0.08	0.17	0.27	0.26
9	0.74	0.05	0.10	0.28	0.89	0.07	0.13	0.22	0.21
10	0.61	0.04	0.08	0.23	0.77	0.07	0.10	0.19	0.18
11	0.86	0.05	0.14	0.36	1.09	0.09	0.18	0.31	0.29
12	0.88	0.05	0.14	0.38	1.10	0.08	0.19	0.29	0.28
13	0.87	0.05	0.15	0.39	1.10	0.09	0.18	0.29	0.27
14	0.76	0.05	0.12	0.29	0.89	0.07	0.15	0.27	0.26
15	0.82	0.04	0.11	0.25	0.91	0.05	0.13	0.20	0.18
16	0.72	0.05	0.11	0.26	0.70	0.04	0.12	0.20	0.19
17	0.77	0.05	0.11	0.26	0.82	0.06	0.13	0.21	0.21
18	0.78	0.07	0.11	0.34	0.84	0.09	0.13	0.26	0.24
19	1.26	0.13	0.20	0.70	1.44	0.17	0.25	0.68	0.66
20	1.18	0.11	0.20	0.67	1.35	0.14	0.26	0.53	0.52
21	1.16	0.10	0.20	0.63	1.29	0.13	0.25	0.51	0.49
22	1.14	0.10	0.21	0.62	1.33	0.12	0.26	0.52	0.50
23	1.15	0.09	0.20	0.60	1.34	0.13	0.25	0.54	0.52
24	1.21	0.09	0.20	0.60	1.39	0.12	0.25	0.49	0.48
25	1.24	0.09	0.19	0.55	1.48	0.13	0.25	0.46	0.46
26	1.08	0.09	0.20	0.56	1.30	0.13	0.27	0.50	0.48
27	1.08	0.09	0.20	0.56	1.29	0.12	0.25	0.49	0.48
28	1.08	0.09	0.20	0.57	1.23	0.12	0.25	0.49	0.48
29	1.13	0.10	0.20	0.61	1.26	0.12	0.26	0.54	0.52
30	1.10	0.09	0.20	0.59	1.19	0.12	0.24	0.50	0.48

	DIONEX DX500 - Manual Samples				Agilent 750ce - Manual Samples				
	Na	K	Mg	Ca	Na	K	Mg	^{43}Ca	^{44}Ca
1	1.04	0.11	0.21	0.59	0.81	0.08	0.17	0.44	0.45
2	1.07	0.10	0.21	0.62	0.85	0.08	0.17	0.46	0.45
3	0.95	0.09	0.21	0.60	0.78	0.08	0.17	0.41	0.41
4	0.97	0.09	0.21	0.58	0.84	0.08	0.18	0.43	0.41
5	0.84	0.08	0.18	0.56	0.83	0.08	0.18	0.41	0.40
6	1.00	0.09	0.20	0.60	0.92	0.10	0.18	0.43	0.43
7	1.10	0.10	0.22	0.63	0.96	0.10	0.19	0.47	0.46
8	1.13	0.13	0.22	0.69	1.02	0.11	0.20	0.49	0.48
9	1.16	0.11	0.22	0.67	1.01	0.10	0.19	0.49	0.48
10	1.17	0.11	0.20	0.63	1.07	0.11	0.20	0.51	0.51
11	0.87	0.08	0.16	0.54	1.14	0.13	0.20	0.53	0.54
12	0.76	0.08	0.13	0.54	1.31	0.16	0.21	0.60	0.60
13	0.48	0.07	0.10	0.25	0.45	0.08	0.08	0.16	0.16
14	0.57	0.05	0.11	0.24	0.60	0.06	0.10	0.18	0.18
15	0.71	0.05	0.15	0.33	0.66	0.06	0.12	0.21	0.21
16	0.42	0.03	0.08	0.20	0.57	0.05	0.10	0.18	0.18
17	0.56	0.04	0.11	0.25	0.56	0.06	0.10	0.18	0.18
18	0.68	0.05	0.13	0.33	0.68	0.06	0.12	0.25	0.25
19	0.55	0.04	0.12	0.31	0.71	0.07	0.14	0.28	0.29
20	0.78	0.06	0.16	0.39	0.72	0.07	0.14	0.27	0.28
21	0.56	0.05	0.11	0.30	0.53	0.06	0.09	0.20	0.19
22					0.51	0.05	0.08	0.18	0.18
23	0.68	0.05	0.13	0.33	0.57	0.05	0.11	0.22	0.22
24	0.74	0.06	0.15	0.39	0.60	0.05	0.12	0.27	0.27
25	0.71	0.06	0.14	0.38	0.63	0.06	0.12	0.30	0.30
26	0.82	0.07	0.17	0.46	0.67	0.06	0.14	0.34	0.32
27	0.60	0.05	0.13	0.36	0.67	0.05	0.14	0.35	0.35
28	0.49	0.04	0.11	0.34	0.70	0.06	0.15	0.38	0.38
29	1.13	0.10	0.20	0.62	0.83	0.07	0.16	0.46	0.46
30	1.00	0.09	0.19	0.59	0.77	0.08	0.15	0.44	0.43

United Kingdom Environment Agency Data of major ions concentrations in New Forest Rivers and Streams.

Highland Water			Roydon Manor		
Sampling date	Cl (mM)	NO_3 (mM)	Sampling date	Cl (mM)	NO_3 (mM)
14/01/04	0.49	0.0137	14/01/04	0.52	0.03
11/02/04	0.66	0.0173	11/02/04	0.72	0.06
10/03/04	0.79	0.0137	10/03/04	0.87	0.08
21/04/04	0.59	0.0137	21/04/04	0.66	0.03
25/05/04	0.74	0.0194	25/05/04	0.88	0.19
24/06/04	0.75	0.0187	24/06/04	0.75	0.06
28/07/04	0.74	0.0166	28/07/04	1.37	0.53
23/08/04	0.72	0.0140	23/08/04	0.91	0.15
22/09/04	0.75	0.0140	22/09/04	0.90	0.13
21/10/04	0.54	0.0297	21/10/04	0.54	0.04
16/11/04	0.75	0.0140	16/11/04	0.83	0.08
15/12/04	0.78	0.0140	15/12/04	0.86	0.09
12/01/05	0.74	0.0169	12/01/05	0.78	0.04
03/02/05	0.76	0.0140	03/02/05	0.83	0.07
23/03/05	0.92	0.0261	23/03/05	0.90	0.04
20/04/05	0.79	0.0140	20/04/05	0.81	0.04
19/05/05	0.79	0.0140	19/05/05	0.88	0.13
10/06/05	0.74	0.0140	10/06/05	0.94	0.15
12/07/05	0.95	0.0154	12/07/05	0.97	0.04
08/08/05	0.69	0.0140	08/08/05	1.15	0.28
05/09/05	0.73	0.0140	05/09/05	1.49	0.50
05/10/05	0.81	0.0247	05/10/05	1.26	0.24
02/11/05	0.55	0.0261	02/11/05	0.62	0.02
01/12/05	0.79	0.0197	01/12/05	0.97	0.13
03/01/06	0.91	0.0247	03/01/06	0.95	0.05
01/02/06	0.85	0.0247	01/02/06	0.97	0.11
04/03/06	0.78	0.0340	04/03/06	0.99	0.10
12/04/06	0.82	0.0140	12/04/06	0.87	0.03
17/05/06	0.81	0.0140	17/05/06	0.85	0.04
09/06/06	0.82	0.0183	09/06/06	1.06	0.21
10/07/06	0.83	0.0154	10/07/06	1.15	0.25
19/10/06	0.88	0.0290	14/08/06	2.00	0.83
01/11/06	0.88	0.0190	19/10/06	1.06	0.15
27/11/06	0.71	0.0494	01/11/06	0.94	0.07
13/12/06	0.85	0.0276	13/12/06	0.92	0.05
21/12/06	0.87	0.0254			
22/01/07	0.78	0.0197			
20/02/07	0.78	0.0176			
23/03/07	0.81	0.0169			
11/04/07	0.83	0.0140			
10/05/07	0.86	0.0261			
08/06/07	0.80	0.0176			
11/07/07	0.71	0.0140			

09/08/07	0.72	0.0140
07/09/07	0.83	0.0140
04/10/07	0.81	0.0140
13/11/07	0.83	0.0140
07/12/07	0.65	0.0140
10/01/08	0.74	0.0204
07/02/08	0.74	0.0140
07/03/08	0.81	0.0140
09/04/08	0.83	0.0140
08/05/08	0.75	0.0140
04/06/08	0.53	0.0140
01/07/08	0.79	0.0154
07/08/08	0.80	0.0140
11/09/08	0.63	0.0140
09/10/08	0.68	0.0140
13/11/08	0.73	0.0161
17/12/08	0.76	0.0190
20/01/09	0.72	0.0261
25/02/09	0.76	0.0140
18/03/09	0.75	0.0140

Balmer Lawn		Whitley	
Sampling date	NO_3 (mM)	Sampling date	NO_3 (mM)
14/01/04	0.0216	14/01/04	0.0214
11/02/04	0.0337	11/02/04	0.0430
10/03/04	0.0223	10/03/04	0.0580
21/04/04	0.0137	21/04/04	0.0194
25/05/04	0.0237	25/05/04	0.1557
24/06/04	0.0137	24/06/04	0.1357
28/07/04	0.0137	28/07/04	0.5200
23/08/04	0.0140	23/08/04	0.1307
22/09/04	0.0140	22/09/04	0.1321
21/10/04	0.0204	21/10/04	0.0233
16/11/04	0.0140	16/11/04	0.0645
15/12/04	0.0140	15/12/04	0.0914
12/01/05	0.0204	12/01/05	0.0283
03/02/05	0.0197	03/02/05	0.0821
23/03/05	0.0240	23/03/05	0.0519
20/04/05	0.0140	20/04/05	0.0596
19/05/05	0.0140	19/05/05	0.1693
10/06/05	0.0140	10/06/05	0.1143
12/07/05	0.0154	08/08/05	0.2414
08/08/05	0.0140	05/09/05	0.4729
05/09/05	0.0140	05/10/05	0.1907
05/10/05	0.0140	14/10/05	0.1607
14/10/05	0.0140	02/11/05	0.0233
01/12/05	0.0254	01/12/05	0.0709

12/12/05	0.0326	03/01/06	0.0467
03/01/06	0.0304	01/02/06	0.1114
01/02/06	0.0297	04/03/06	0.0957
04/03/06	0.0404	12/04/06	0.0383
12/04/06	0.0161	17/05/06	0.0666
17/05/06	0.0154	09/06/06	0.2029
09/06/06	0.0261	10/07/06	0.1300
10/07/06	0.0476	14/08/06	1.2786
14/08/06	0.0140	19/10/06	0.1050
19/10/06	0.0283	01/11/06	0.1343
01/11/06	0.0254	27/11/06	0.0418
27/11/06	0.0354	13/12/06	0.0404
13/12/06	0.0347	10/05/07	0.1564
		09/08/07	0.1286
		13/11/07	0.1564
		13/02/08	0.0639
		08/05/08	0.0709
		11/09/08	0.0533
		13/11/08	0.0447
		25/02/09	0.0694

Laboratory evaluation of the contribution of the rhodamine solution on the samples.

Based on the fact that the micro solenoid pump injects 50 μl in approximately 1 ml of sample, we have mixed 250 μl of rhodamine solution with 5 ml of deionized water (volumetric addition) and the samples were analyzed on the DX500 system for major anions and cations. Values of 0.0 indicate that the concentration was below the method's detection limit.

	Concentrations in mM						
	Cl^-	SO_4^{-2}	NO_3^-	Na^+	K^+	Mg^{+2}	Ca^{+2}
Sample 1	0.099	0.017	0.0	0.054	0.0	0.0	0.0
Sample 2	0.101	0.019	0.0	0.052	0.0	0.0	0.0
Sample 3	0.092	0.021	0.0	0.047	0.0	0.0	0.0

Analysis of deionized water samples that passed through the corrugated plates that were used to collect rainwater. Samples were analyzed on the DX500 Ion Chromatography system. Values are below the method's detection limit.`

Blanks from rainwater collection system

	Concentrations in μM						
	Cl^-	SO_4^{-2}	NO_3^-	Na^+	K^+	Mg^{+2}	Ca^{+2}
30/04/2008	0	0	0	0	0	0	0
09/07/2008	0	0	0	0	0	0	0