

# Titan: A new facility for ultraclean sampling of trace elements and isotopes in the deep oceans in the international Geotraces program

H.J.W. De Baar<sup>a,b,\*</sup>, K.R. Timmermans<sup>a</sup>, P. Laan<sup>a</sup>, H.H. De Porto<sup>a</sup>, S. Ober<sup>a</sup>,  
J.J. Blom<sup>a</sup>, M.C. Bakker<sup>a</sup>, J. Schilling<sup>a</sup>, G. Sarthou<sup>c</sup>, M.G. Smit<sup>a</sup>, M. Klunder<sup>a</sup>

<sup>a</sup> Royal Netherlands Institute for Sea Research, Texel, The Netherlands

<sup>b</sup> Department Ocean Ecosystems, Centre for Ecological and Evolutionary Studies, University of Groningen, The Netherlands

<sup>c</sup> Institut Universitaire Européen de la Mer, Brest, France

Received 7 October 2006; received in revised form 22 July 2007; accepted 24 July 2007

Available online 2 August 2007

---

## Abstract

Towards more rapid ultraclean sampling of deep ocean waters for trace elements, a novel rectangular frame was constructed of titanium, holding two rows of 12 samplers, as well as various sensors. The frame is deployed to deep ocean waters by an 8000 m length Kevlar wire with internal power and signal cables. Closing of each sampler is by seawater hydraulics via silicone tubings connecting each sampler with a central 24 position Multivalve. Upon recovery the complete frame with 24 samplers is placed inside an ultraclean laboratory van, where water is drawn via filters into bottles. Previously the clean sampling of ocean waters has been very time-consuming by attachment of individual ultraclean bottle samplers one by one to a metal-free (e.g. all-Kevlar) hydrowire. The novel Titan system is 3–4 times faster and permits routine collection of deep ocean sections while economizing required shiptime. In a test of the new system in November 2005 in the Canary Basin excellent low dissolved Fe concentrations (~0.1 to ~0.4 nM) are consistent with values obtained of individual samplers on a simple wire, and previous values in a pilot study of 2002 in the same basin, as well as published dissolved Fe values elsewhere in the northeast Atlantic Ocean.

© 2007 Elsevier B.V. All rights reserved.

*Keywords:* Sampling; Clean; Titanium; Trace metals; Oceans

---

## 1. Introduction

The distribution of trace metals and other trace elements in the world oceans has been, and still is, one of the grand challenges in oceanography. Having been encouraged by remarkable findings of metal-rich hot salty waters at the bottom of the Red Sea (Brewer et al.,

1965), soon attention was focused on the remarkable chemistry in anoxic waters of the Black Sea. Here a dramatic increase of dissolved manganese (Mn) was found going from about 0.5–5 nM within the oxic surface waters to as high as a maximum of about 8–9 μM in the anoxic deep waters (Spencer and Brewer, 1971). In later expeditions these values and remarkable trends for dissolved Mn were nicely confirmed and further investigated (Haraldsson and Westerlund, 1988; Lewis and Landing, 1991). Similarly the dissolved iron (Fe) showed a strong increase, albeit less dramatic than Mn, from the oxic into the deeper anoxic waters (Spencer and Brewer, 1971) of the Black Sea. In the later studies this

---

\* Corresponding author. Royal Netherlands Institute for Sea Research, Texel, The Netherlands. Tel.: +31 222 369465; fax: +31 222 319674.

E-mail address: [debaar@nioz.nl](mailto:debaar@nioz.nl) (H.J.W. De Baar).

trend was also reported, with varying depths and intensities of the dissolved Fe maximum (Haraldsson and Westerlund, 1988; Lewis and Landing, 1991).

### 1.1. The GEOSECS program

Thus when the very ambitious GEOSECS program started, the sampling and detection of a suite of trace elements (Fe, Cu, Zn, Co, Sb, Cs and U) was also vigorously pursued at an initial GEOSECS-II test station (Brewer et al., 1972). However these earliest results have eventually become superseded (Campbell, 1983) by the first reliable data collected some years later. The increased awareness of the need for clean techniques of sampling, filtering and analyzing seawater for trace metals, led to the criterion of oceanographic consistency, as first mentioned for Cu versus nutrients in surface water samples collected along a transect (Boyle and Edmond, 1975). Next, the first convincing vertical profiles of dissolved metals Cd (Boyle et al., 1976), Ni (Sclater et al., 1976), Mn (Bender et al., 1977), Cu (Boyle et al., 1977), and Al (Hydes, 1979) were reported. These later GEOSECS samples (Campbell, 1983, his Table 44.2) were collected with standard 30 L Niskin samplers mounted on a Rosette. Nevertheless routine sampling and analyses still were extremely difficult, and within the GEOSECS program complete ocean vertical section distributions for trace elements were realized merely for one: the apparently less contamination-prone ‘non-metallic’ earth-alkaline element Ba (Bender et al., 1972; Bacon and Edmond, 1972; Chan et al., 1977). Moreover the sampling system did not permit (Bruland, 1983) uncontaminated samples to be collected for certain very contamination-prone trace metals, notably Zn (Bruland et al., 1978), Fe or Pb.

### 1.2. Clean sampling for Pb

Quite independently the zealous and successful efforts of Clair Patterson to determine lead (Pb) in seawater, led to development of a new deep-water sampler with which samples could be collected free from contamination by the ship and hydrowire (Schaule and Patterson, 1981). This allowed Patterson and co-workers to quantify and understand the natural cycling of Pb in the exterior biosphere of our precious planet, and discover the major perturbations of this cycle due to severe global contamination by mankind. In combination with his previous first-ever reliable dating of the 4.55 million years age of the whole planet by Pb isotopes (Patterson, 1956), the achievements and contributions of Patterson cannot be underestimated; yet outside the scientific community they have been (Bryson, 2004).

### 1.3. Clean sampling for several metals

The deep-sea sampler of Patterson and Schaule was a marvelous breakthrough, yet each time-consuming lowering yields only one sample to be collected. However Bruland et al. (1979) took another approach by mounting several internally Teflon-coated GO-FLO (General Oceanics) non-metallic water samplers one-by-one on a Kevlar (non-metallic) hydrowire. By detailed comparison with Patterson’s sampler no significant differences were observed for Zn, Cu, Ni and Cd (Bruland et al., 1979). Soon afterwards the classical article on these four trace metals and their co-variances with major nutrients did appear (Bruland, 1980). This was followed by the first-ever reliable data on dissolved Fe (Landing and Bruland, 1981) as confirmed soon afterwards relying on the same Teflon-coated GO-FLO sampler approach (Gordon et al., 1982) and eventually published (Landing, 1983; Landing and Bruland, 1987). All previous reported values of dissolved Fe in seawater, from year 1874 onwards (as reviewed by De Baar, 1994) had become obsolete. The approach of mounting several individual GO-FLO samplers, one after another, on the Kevlar hydrowire was more efficient than doing one sample at a time, and has become the standard method for sampling trace metals (trace elements) in the oceans.

This article is focused on trace-metal-clean sampling devices. Nevertheless one must realize that breakthroughs were also very much dependent on the awareness of inadvertent contamination by common plastics (e.g. Patterson and Settle, 1976; Moody and Lindstrom, 1977), and the parallel developments of several clean analytical methods, notably the very successful dithiocarbamate/solvent extraction procedure (Kinrade and van Loon, 1974; Danielsson et al., 1978; and independently Bruland et al., 1979).

The revolutionary 1975–1983 era led to discoveries of several more ‘oceanographically-consistent’ vertical profiles of many trace elements, for example of Ce and the other lanthanides, independently by Elderfield and Greaves (1982) and by the group of Peter Brewer (De Baar et al., 1983, 1985). With the comfort of hindsight we now realize that the review by Brewer (1975) on minor elements in sea water, did appear in print one year before the revolution started (Boyle et al., 1976), and the quantum leap in knowledge of trace elements necessitated a new review chapter within less than a decade (Bruland, 1983).

### 1.4. The Fe age in oceanography

Just a few years later Fe was shown to be a limiting trace element for phytoplankton growth, first in the

subArctic Pacific Ocean (Martin and Fitzwater, 1988) and then in the Southern Ocean (De Baar et al., 1990). Nowadays we know that not only Fe, but also Zn and various other first-row transition metals are essential for life in the sea, and shown or suspected to be available in low concentrations limiting for phytoplankton growth (e.g. review of De Baar and La Roche, 2003). The 1990–2000 period was perhaps the “Iron Age in Oceanography” (Coale et al., 1999), and novel methods were developed for shipboard analyses of Fe (Obata et al., 1993; Measures et al., 1995; De Jong et al., 1998, 2000; Bowie et al., 1998, see also in Bowie et al., 2006; Johnson et al., 2007) and several other metals, or for potentially higher accuracy of Fe by isotope dilution mass spectrometry (Wu and Boyle, 1998; Saito and Schneider, 2006).

### 1.5. Alternative clean sampling approaches

Over the years there have been some other sampling devices, like the teflon Mercos sampler used in surface waters (Freimann et al., 1983), the very successful underway pump sampling from a torpedo towed alongside the ship (De Jong et al., 1998) which nowadays is used routinely by several scientists, or the moored *in situ* MITESS sampler (Bell et al., 2002; Bergquist and Boyle, 2006). Two titanium frames, each holding 24 water samplers (10 L, OTE, <http://www.oceantestequip.com/watersampler.html>), exist in Britain (U.K.) ([www.bodc.ac.uk/data/online\\_delivery/amt/document/amt12\\_ctd.pdf](http://www.bodc.ac.uk/data/online_delivery/amt/document/amt12_ctd.pdf)). First use of such titanium frame was in 2001 aboard RV Charles Darwin (CD128 cruise). Recently a stainless steel cable has become available, the ca. 15 m above the frame are taped off, and closing of samplers is done in the downcast (Rijkenberg, pers. comm.).

Moreover a titanium armored cable (diameter 8.39 mm) of ca. 11 km length is being used on R.V. Hakuho-maru (Ocean Research Institute, University of Tokyo), while such cable of ca. 3500 m length is available on R.V. Umitaka-maru (Tokyo University of Marine Science and Technology). Usually this Ti cable is combined with a CTD-Rosette or CTD-Carousel frame holding Teflon-coated Niskin samplers which are lever-action type Niskin or Niskin-X (General Oceanics, Inc.). These systems have been used successfully for sampling of various trace elements and isotopes (e.g. Obata et al., 1997, 2004; Amakawa et al., 2004).

### 1.6. Rationale

Nevertheless almost all high quality deep ocean data reported in the past twenty years has been collected using the suite of single GO-FLO samplers on a Kevlar

hydrowire (Bruland et al., 1979). The latter now classical/standard approach of mounting individual GO-FLO samplers one by one on a Kevlar hydrowire still is very laborious and time-consuming. Also upon recovery the samplers have to be hand-carried one by one over the open deck of the ship to a clean-air laboratory container. Thus despite more than two decades of research, the overall database of dissolved trace metals in seawater still is very modest. For example, for dissolved Fe, the complete published literature until early 2001 (De Baar and de Jong, 2001) still is inconclusive with regards to its oceanic distribution. Since then a few more deep water profiles have been reported (e.g. summarized by Gregg et al., 2003; Parekh et al., 2005; more recent data by Boyle et al., 2005; Chase et al., 2006). However still only very few deep water Fe data exist (GEOTRACES Science plan), let alone complete deep sections. Moreover without a systematic sampling of complete profiles and sections, it is difficult to apply the criterion of oceanographic consistency for verification. Hence until today questions remain about accuracy of the available data of dissolved Fe in the literature. On the one hand this has led to a drive for intercomparison and certification (IOC, Landing et al., 1995; IRONAGES, Bowie et al., 2003, 2006; SAFE, Johnson et al., 2003, 2007). On the other hand, far more intensive sampling of the oceans is required in order to arrive at reliable oceanic distributions of trace nutrients like Fe or Zn, akin to and inspired by the reliable distributions of major nutrients nitrate, phosphate and silicate achieved in the GEOSECS program of the 1970's.

### 1.7. Objectives

Towards more efficient operations in the GEO-TRACES program (Geotraces, 2006) of the next decade, here we report on the research, development and verification in 2002–2005 of a more efficient and reliable sampling approach for the deep oceans. This was done in the wider context of the IRONAGES program, where the 2000 IRONAGES-1 cruise for intercalibration and certification (Bowie et al., 2003, 2006) was followed by the March 2002 IRONAGES-2 “Iron from Below” cruise (Laëš et al., 2003, 2007; Ussher et al., 2007), and the October 2002 IRONAGES-3 “Iron from Above” cruise (Kramer et al., 2003, 2004; Sarthou et al., 2003, 2007; Gerringa et al., 2006). During IRONAGES-3 (October, 2002) a pilot frame of coated stainless steel was successfully used throughout the 4000 m deep water column, and findings for dissolved Fe and Al were presented in April 2003 (Sarthou et al., 2003; Kramer et al., 2003) and published afterwards (Kramer et al., 2004; Sarthou et al., 2007). Finally the novel Titan system

holding 24 GO-FLO samplers was tested in a dedicated October 2005 cruise, and preliminary results have been presented within year 2006 (Timmermans et al., 2006). Meanwhile in July–August 2003 the UK titanium frame was deployed successfully for dissolved Fe measurements along a transect across the Celtic Sea shelf break (Nédélec et al., 2007; with OTE samplers with external springs; conventional CTD cable taped off several metres above the frame, Statham, pers.comm.). Moreover in August 2003 a coated Al frame holding 12 GO-FLO samplers, similar to our 2002 pilot frame of coated stainless steel, was used for sampling the upper 1000 m along CLIVAR section A16 for and results of dissolved Fe and Al presented in February 2004 (Landing et al., 2004).

## 2. Materials

### 2.1. Samplers

Individual 12 L PVC GO-FLO samplers (General Oceanics Inc.) have been modified by replacement of the spigot by an all-teflon valve (Cole Parmer: PN A-06392-31), and by spraying the interior with a teflon coating. Upon recovery the bleeding valve screw-plug at the top end of the sampler is replaced by a connector to a nitrogen gas line for pressurizing the sampler as to enhance the seawater filtration. The original black rubber springs loose their tension strength by ageing and in cold ( $\sim 2^\circ\text{C}$ ) deep waters and even colder Antarctic waters. This leads to more failures of complete bottle closing. Moreover the black rubber contains a variety of contaminants. Therefore special long coiled springs of seawater-corrosion-resistant stainless steel SS 316 have been installed. Alternatively silicone rubber tubing can also be used as tension springs. For those samplers placed permanently on the titanium frame, the mounting appendices on each sampler were replaced by a titanium mounting plate, being attached to the frame with two titanium bolts.

### 2.2. Seven millimetre hydrowire, winch and messengers

The 4000 m length 7 mm diameter hydrowire consists of a braided Kevlar 29 core with a braided polyester jacket mantle, and is spooled on a 36 cm diameter drum until a final 60 cm, on a simple oceanographic winch (weight winch is 4500 kg). For tripping samplers mounted individually on this single Kevlar hydrowire, all-teflon messenger weights were used, with internal stainless steel ballast and internal stainless spring-loaded fixation pin (Fig. 1).

### 2.3. Seventeen millimetre CTD cable

The 17.7 mm diameter hydrowire was designed with 7 independent internal signal/conductor cables of 0.25 mm each, together within a 5 mm diameter surrounded by Kevlar strands and protected by an external 2.5 mm thick Hydrel jacket. Some 8000 m length of this cable was manufactured by Cousin trestec

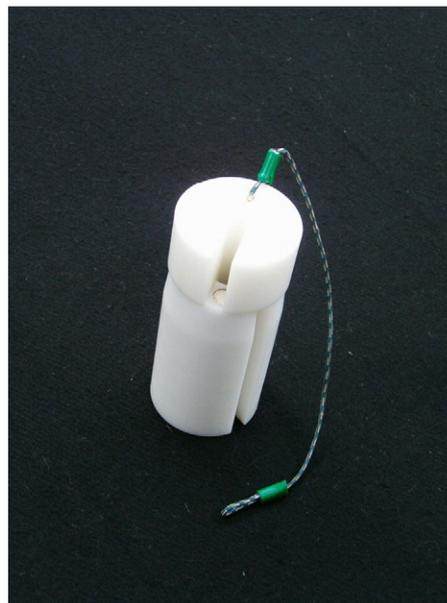


Fig. 1. Messenger of plastic Delrin (Dupont) for tripping single GO-FLO samplers mounted on a seven millimetre Kevlar hydrowire. The bottom part (60 mm diameter, 100 mm height) has one central vertical opening throughout (diameter 20 mm), six vertical drill holes (diameter 11 mm, depth 90 mm) in which are placed six stainless steel rods as ballast which are plastic-sealed on top, and a seventh smaller drill hole (diameter 6 mm, depth 40 mm) holding a spring-(17 mm length)-loaded pin (length 28 mm) with rounded top. The top part (60 mm diameter, 35 mm height) has a central extension pipe (external diameter 19 mm, internal diameter 8 mm, open at one side over its full 95 mm length) which fits inside central opening of bottom part. Two dents allow spring-loaded pin to fall into two positions at  $90^\circ$  angle, for full open when placing around hydrowire, or top closed around hydrowire. Stainless steel bolt at rear centre of lower part enters into  $90^\circ$  sleeve of central extension pipe of top part for holding two parts together while allowing the  $90^\circ$  mutual rotation. Kevlar line with loop for attaching one messenger at bottom release hook of each mounted GO-FLO sampler.

S.A. (France) according to our specifications. The tension strength of the cable is 16,000 kg which allows maximum payload of 9000 kg, more than the below described ultraclean sampler frames. The cable is spooled on a 190 cm diameter drum until a final 260 cm diameter, of an oceanographic traction winch (Fig. 2) specifically designed and built by Kley (France) 30, Boulevard Bellerive; 92566 Rueil Malmaison, France (<http://www.kleyfrance.fr/>). Complete design criteria and drawings are available upon request.

### 2.4. Sheaving block

The 17.7 mm cable is led over a large diameter (110 cm, thickness 94 mm) wheel into the sea. The large diameter of the wheel (cut from a cast sheet (100 mm thickness) of polyamide Ertalon 6PLA, <http://www.eriks.nl/>) is required to minimize shear stress among the Kevlar strings within the cable which would cause decreasing overall tension strength of the cable.



Fig. 2. Kley France winch. Specification: 20 Foot (ISO 1C20') container; external length: 6060 mm; external width: 2440 mm; external height: 3258 mm; weight: 22000 kg. Not shown is the Powerpack for Kley-France winch to be placed within 10 m cables length of actual winch: 10 Foot (ISO D 10') container; external length: 2991 mm; external width: 2440 mm; external height: 2591 mm, weight: 5000 kg; powersupply: 3 Phase 380 V, 50 Hz, 200 Amp. Investment cost of winch is ca. € 400,000 – plus ca. US \$ 200,000 – for the Kevlar cable.

The wheel has a groove in the middle for the cable, such that the cable will never get in touch with the wheels frame. The wheel is suspended from either the high A-frame amidship starboard (RV Pelagia) or an extendable load-arm at the starboard aft-deck of Polarstern.

### 2.5. Pilot Rosette frame

For the pilot study in autumn 2002 a simple hexagonal CTD/Rosette frame was designed (Fig. 3) and built of a stainless steel alloy SS 316 selected for optimal corrosion-resistance in seawater, and once assembled by electric welding with Filarc RS316LC-P welding rods the complete frame was cleaned by blasting with non-metallic Sa2.5 grit, then coated with a dual layer Epoxy consisting of 60 Mu epoxypowder primer and next 60–80 Mu polyester powdercoating. The powdercoatings are fixed to the frame by melting, by placing the frame with powder in an oven at 200 °C. The seawater-resistant alloy does not require an additional sacrificial anode of e.g. zinc (Zn) which would in itself be a conceivable source of Zn contamination. The actual CTD sensors-package as well as other sensors (e.g. optics) all are in titanium housings.

### 2.6. Hydraulics

For triggering of the individual samplers, each sampler was equipped with a hydraulic-seawater-driven release unit (Fig. 4a) which via silicone rubber tubing (6 mm internal, 12 mm external diameters) are connected to a central 24-positions rotating Multivalve device (Fig. 4b), in turn driven by an electric servomotor (in titanium house) which is controlled via the modem-

channel of the SBE-9/11+CTD running Seasafe for Windows (Ober et al., 2002). Each release unit comprises a piston with tension spring, and driving the release of a cable hook. Before deployment each of the 24 release units and its connecting silicone tubing is evacuated on shipboard with a vacuum line; as a result the internal spring is compressed and the piston in upmost position; all GO-FLO samplers are closed; the trip wires of each GO-FLO are led over the pressure device of the GO-FLO itself and then hooked to the cable hook. Upon deployment the samplers go in closed position across the air/sea interface, next the standard pressure devices of the GO-FLO samplers actuate at about 1 atm overpressure (i.e., at about 10 m depth) and all samplers are opened. During the upcast, once at sampling depth, the rotating device of the Multivalve is actuated, by opening one of its 24 valves the ambient seawater is allowed into the silicone tubing towards the release unit, there the seawater fills the vacuum space above the piston which is pushed down by the spring, and the hook is released, thus releasing the GO-FLO trip wire.

### 2.7. Titanium frame

The GEOTRACES program aims at many of the 92 existing chemical elements and their isotopes. Inevitably a sampling system has to be constructed of at least one chemical element. Given the major scientific attention for chemical elements Fe and Al, these were deemed less suitable for construction of a frame. Upon consideration of various materials including carbon-fibre reinforced plastics, eventually pure titanium (Ti) was chosen. The element Ti is in itself of geochemical interest (Skrabal, 2006), notably as a source tracer of continental matter, yet one assumes that a study of Ti in the oceans may rely on a



Fig. 3. Pilot Rosette with 4 modified GO-FLO samplers on left side, each with white plastic release-unit connected via silicone tubing with central rotating device shown at top right. Notice the loose tubing hanging over the frame which is connected to ships vacuum line, and used to draw vacuum in the whole system when on deck, as a result the piston in each release unit is sucked into the high position. (The two light-gray NOEX samplers of NIOZ are not ultraclean but otherwise such samplers have been used routinely for many years in combination with the hydraulics for tripping/closing.)

conventional standard stainless steel CTD/Rosette sampling system (e.g. Fig. 3) where regular Niskin or NOEX (Fig. 3) samplers may in fact be adequate.

The hydraulics Multivalve and trip-system allowing any shape of frame beyond the traditional (semi-) circular led to the design of a rectangular frame holding two rows of 12 samplers each (Fig. 5) which could be placed inside a laboratory van of standard sea-container dimensions. In the lower middle of the frame are mounted a CTD (Seabird 9-/11plus) complete with its sensors, all within all-titanium housings and an optical backscatter unit (OBS, Seapoint) in its own plastic housing. Moreover there are ballast weights to ensure adequate tension strength on the cable during lowering. Titanium boxes were filled with 500 kg lead (Pb) ballast and sealed by Ti-welding, and mounted as low as possible, for optimal stability when the frame is transported over the ships deck. The frame stands on four polyurethane wheels (20 cm diameter) and upon recovery from the sea is placed on a special carriage mounted on a manpowered hydraulic long-bed fork-lift. The whole assembly is driven over the ships deck to the front door of the container van, upon which the titanium frame is pushed into the container, and finally the door closed. In the process the titanium frame never directly comes in contact with the ships deck. Once in the laboratory the frame is fixed in place by titanium floor-clamps.

## 2.8. Ultraclean air laboratory container van

This laboratory was designed (Fig. 6) with an incoming clean air downflow exactly over the position of the titanium frame with samplers. The exit air flow is over the floor into two low benches along each side and then back into the technical room where the air is recirculated over the various HEPA filters (F-7 pre-filter, F-9 final filter; CEN, 2002), as well as passing an air-conditioning unit towards achieving stable temperature. During each cycle about 12% of the air was set to be replaced by new air drawn in from outside, this replacement/recycling ratio is adjustable. Briefly at an overall renewal rate of  $1800 \text{ m}^{-3} \text{ hour}^{-1}$ , and given the required replacement volume of  $50 \text{ m}^3 \text{ hour}^{-1} \text{ person}^{-1}$  the  $150 \text{ m}^3 \text{ hour}^{-1} \text{ person}^{-1}$  or 12% allows 3 persons working in the laboratory, although normally only 1–2 persons are in the room. The air-conditioning allows the cleanroom temperature to be set anywhere between  $5 (\pm 1)$  and  $20 (\pm 1) ^\circ\text{C}$ .

The acceptance tests of the clean room for international (ISO) Class-7 (as off 2001 replacing the US Federal Standard 209E Cleanroom Class 10,000) were certified by using a MetOne 3313 laser optics particle counter positioned inside the laboratory. During stable operation the particle count at 110 cm height was 12 particles  $\text{m}^{-3}$  of the size class  $>0.5 \mu\text{m}$  and nil particles  $\text{m}^{-3}$  of size class  $>5 \mu\text{m}$ . Similarly at 20 cm height this was  $6 \pm 8$  particles  $\text{m}^{-3}$  of the size class  $>0.5 \mu\text{m}$  and nil particles  $\text{m}^{-3}$  of size class  $>5 \mu\text{m}$ . The recovery time was tested by a smoke generator which brings the particle count as high as  $7,000,000$  particles  $\text{m}^{-3}$  of the size class  $>0.5 \mu\text{m}$ . Next this particle generator was turned off, and within 90 s the particle counts had dropped over six orders of magnitude down to 1 particle  $\text{m}^{-3}$  of the size class  $>0.5 \mu\text{m}$  (not shown). In fact this is within the more stringent criteria of an ISO Class 6 clean room (formerly US FED STD 209E Class 1000).

Each GO-FLO sampler is at its high end connected via silicone tubings to a nitrogen ( $\text{N}_2$ ) gas line which is supplied via a filter cartridge ( $0.45 \mu\text{m}$ , Sartorius, Midisart 2000) from an instrument grade (top-grade 5.0; <https://www.lindegasonline.nl/xgis/pib/NL-PIB0026.pdf>)  $\text{N}_2$  gas cylinder. The lower teflon seawater drain valves are connected with PTFE tubing and sort silicone connector to the (Sartrobran-300, Sartorius) filtration cartridges.

This clean laboratory is used only for drawing seawater from the GO-FLO samplers via the filter cartridge into various (100–1000 ml range) bottles, often the acidification (to pH 1.8) of the bottles, and packaging of each bottle in a plastic bag and then in a plastic crate packed in large bag. The crates of bottles are then brought into other clean air laboratory containers for final shipboard analyses, or stored at room temperature or in the freezer for later analyses in the home laboratory.

## 3. Methods

### 3.1. 2002 Expedition

Seawater samples were collected aboard the R.V. Pelagia between October 3 and October 29, 2002, during the IRONAGES-3 shipboard expedition between Ponta Delgada

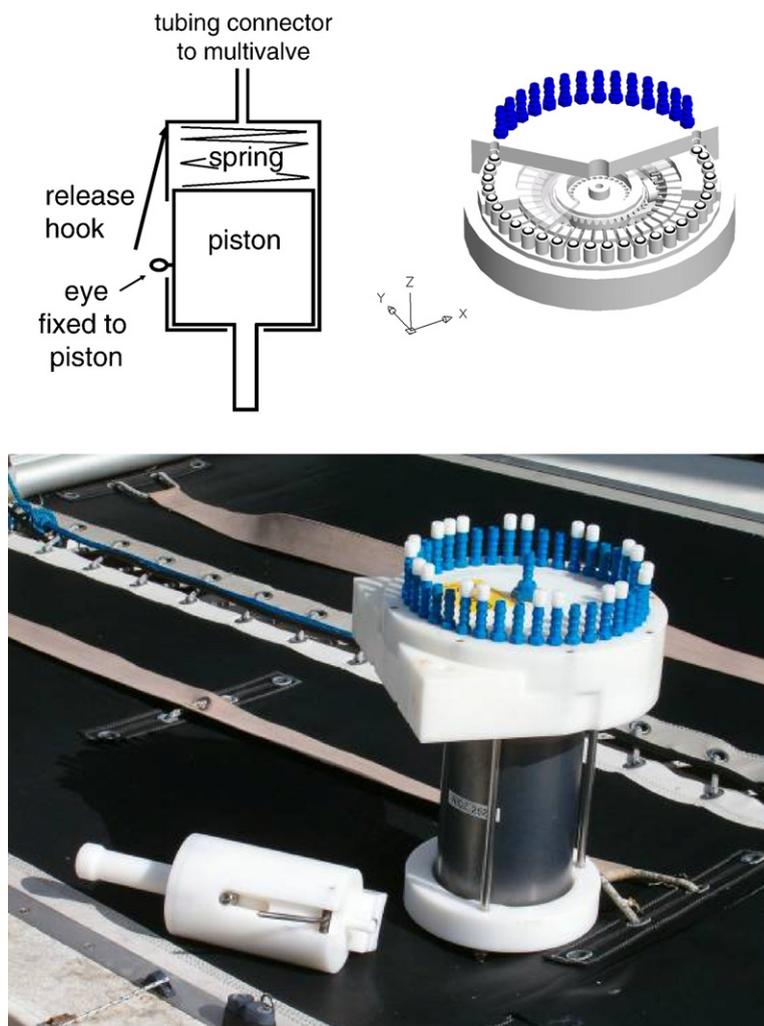


Fig. 4. a) individual release unit; b) inner workings of 24 position multivalve c) photograph of both. Release unit with internal valve and spring; the lanyard of a GO-FLO sampler is hooked to release hook, which is fixed by eye on piston. When water enters on top from multivalve, the spring decompresses, pushing down piston and eyelet, the hook is released and lanyard can slip off. Both the release unit and the multivalve are made of Ertacetal-POMC plastic (<http://www.eriks.nl/>). Details of Multivalve system are available on request.

(Azores, Portugal) and Valencia (Spain). Shallow surface water depth profiles (0–150 m) as well as deep profiles (0–4000 m) were collected at several stations, see [Sarthou et al. \(2007\)](#). Samples for dissolved Fe (DFe, filtered, <math>0.2 \mu\text{m}</math>) concentrations were obtained using the samplers on the Pilot Rosette. Here we only report results of station 34 (30.00°N 17.50°W; 24 October 2002) where one shallow hydrocast (34-1) as well as one deep hydrocast (34-2) were done with the Pilot Rosette. Moreover a third hydrocast (34-3) was done where six (6) GO-FLO samplers were mounted individually on the 7 mm Kevlar hydrowire for comparison with the Pilot Rosette sampling system. Upon recovery the GO-FLO samplers were dismantled from either the Pilot Rosette or the 7 mm Kevlar wire and carried into a clean air laboratory container (latter container not here described). Filtered samples for dissolved Fe analyses were collected from the GO-FLO samplers using slight  $\text{N}_2$  overpressure and filtration

through  $0.2 \mu\text{m}$  filter cartridges (Sartrobran-300, Sartorius). The dissolved Fe concentrations were measured by the NIOZ (P. Laan) using the method of [De Jong et al. \(1998\)](#) which is based on the chemiluminescence method of [Obata et al. \(1993\)](#). The accuracy of the shipboard method of [De Jong et al. \(1998\)](#) and its application ([De Baar et al., 1999](#)) has been deemed to be excellent ([Bruland and Rue, 2001](#)). All analyses were done inside a dedicated clean-air analytical laboratory container. Samples of filtered seawater were left in the dark for about an hour as to ensure all Fe to be in the Fe(III) state, then acidified to pH 1.8 by addition of triple quartz distilled HCl. Following the original method of [De Jong et al. \(1998\)](#) the sample is next re-adjusted to pH  $\sim 4.5$  with ammonium acetate buffer prior to concentrating the iron on a 8-HQ chelating immobilized on a Toyopearl TSK HW40C resin column. Each sample was analyzed in triplicate.



Fig. 5. Side view of frame with rows of GO-FLO samplers, placed on carriage which in turn is placed on a longbed-forklift trolley. Notice white (plastic: Ertacetal-POMC (<http://www.eriks.nl/>)) individual trip device at each GO-FLO sampler, connected with silicone tubing to white 24 positions multivalve unit in lower centre; sensors housings of titanium at middle bottom are mounted left (CTD) and right (optics), the horizontal boxes at the bottom are housing the nylon wheels at each corner of the frame, fixed by breaks operated using the handles on top, as well as the lead ballast. The underlying aluminium carriage can be fork-lifted, see forks at bottom left of photograph. Construction costs of the frame including Titanium materials is ca. € 48.000 – plus ca. € 60.000 – for purchasing of CTD sensors package in its titanium pressure housing (Seabird 9-/11plus). Not included is the purchasing cost of GO-FLO samplers supplied by General Oceanics Inc., Miami, USA.

Moreover at same station 34 (34-1, 34-2 & 34-3), the dissolved Fe in the same samples were analyzed independently onboard with a similar FIA technique of IUEM (G.Sarthou) also based on the Obata et al. (1993) method (Sarthou et al., 2007). This method and its results at several stations during the same IRONAGES-3 cruise have been reported in detail by Sarthou et al. (2007). Previously during the IRONAGES-1 expedition for Fe intercalibration and certification (RV Polarstern ANT XVIII/1, September 29th to October 23rd 2000), the two methods (NIOZ by P.L. Croot and P. Laan; and then UBO now IUEM by then G. Sarthou and S. Blain) had already been compared (Bowie et al., 2003).

Dissolved Aluminium (Al) concentrations were measured concomitantly with dissolved Fe concentrations and the methods and results were published by Kramer et al. (2004).

Samples for dissolved nutrient analysis were collected in a high-density polyethylene sample bottle, filtered through 0.2 µm filter cartridges (Sartrobran-300, Sartorius) and stored in the dark at 4°C in a polyethylene vial. All samples were analyzed within 8 h on a Technicon TRAAcs 800 autoanalyzer, except for some orthosilicic acid samples which were analysed within 24 h. The nutrients were measured colorimetrically after Grasshoff (1983).

### 3.2. 2005 Expedition

The new titanium sampler and its clean container were tested for the first time during Pelagia cruise 64 PE 241, Tuesday 1 November 2005 from Cadiz to Thursday 10 November 2005

arrival at Las Palmas. Upon some trials for general performance and minor mechanical and electronic fine tuning, two complete deep hydrocasts were collected at the same site (30 °N, 17.5 °W) as sampled previously in the 2002 expedition. Upon recovery the complete frame was placed on its own cart and driven to the clean container, upon which it was pushed inside and fixed to the floor with titanium clamps. Next the seawater was filtered directly from each GO-FLO sampler (under N<sub>2</sub> gas pressure) via the 0.2 µm filter cartridges (Sartrobran-300, Sartorius) into sample bottles. Finally the GO-FLO samplers and hydraulics system was set up again, upon which the complete frame remained in the clean container, ready for next deployment. In addition at the same site (30 °N, 17.5 °W) two deep hydrocasts were done with the mounting of individual GO-FLO samplers on the single 7 mm hydrowire. All samples were filtered and analyzed according to the NIOZ method as described above for the 2002 cruise, yet adapted with the following rationale and modifications.

Briefly when adopting the FIA-CL method, we had introduced a stronger acidification step to low pH 1.8 to ensure complete dissolution and dissociation (from organic ligands) of the iron, then mixed the sample with buffer to raise the pH to 4.2 as required for optimal iron affinity of the 8HQ column (De Jong et al., 1998; De Baar et al., 1999). Nevertheless it was realized that “The immobilized 8-HQ has very high affinity to iron and the resulting values are deemed to represent the complete dissolved fraction, although less than 100% extraction efficiency, due to competing very strong natural organic ligands, cannot be ruled out” (De Baar et al., 1999, see also Bruland and Rue,

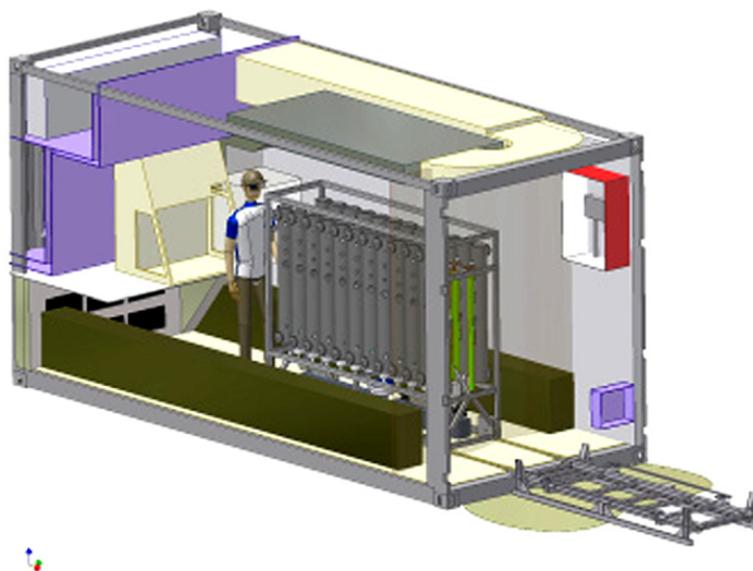


Fig. 6. Computer aided design of the clean air laboratory container, by NIOZ Marine Research Facilities. Creamwhite airduct within the roof brings filtered and temperature-conditioned air into downflow HEPA filter unit exactly over the titanium frame with GO-FLO samplers. At the bottom the air is drafted into two dark-green return flow ducts (also serving as seating benches for the analyst during seawater filtration activity) back into the technical room beyond the purple wall, where the air is filtered again. Workbench at one end holds laminar flow clean air bench for packaging individual sample bottles into one plastic bag and then place these in plastic transport crate standing below the bench. At right hand side is a benchtop refrigerator. Below workbench in the middle is an emergency escape hatch for exit via below the technical compartment; safety rules require two exits i.e. the regular door and the escape hatch. The titanium frame on 4 nylon wheels is pushed from the outside carriage into subducted grooves within the container floor, which also serve as drains for any spilled seawater. Clean-container is a 20 Foot High Cube container; external Length: 6060 mm; external width: 2440 mm; external height: 2895 mm; weight: 8000 kg; powersupply: 240 V, 50 Hz, 16 amp. Coarse 410 V, 50 Hz, 32 amp. Equipped with power supply AC-unit, and seawater connection. Construction by Transmo Container Service B.V., Graanweg 9, 4782PP Moerdijk, The Netherlands (Tel: + 31 (0) 168 38 10 15, Fax:+ 31 (0) 168 38 10 16; Commercial Manager: J. Kooijman j.kooyman@transmo.nl (<http://www.transmo.nl/>). Air-handling systems by Goldwell Airconditioning B.V., Koningsweg 20-4, 3762 EC SOEST, The Netherlands, Tel: 0031+35- 60 333 60, Fax: 0031+35- 60 333 58, info@goldwell.nl (<http://www.goldwell.nl/>). Details of the Titan and Multivalve systems are available on request to Royal NIOZ (<http://www.nioz.nl>). Construction cost of the container laboratory is ca. 135.000 — including all materials and the separate aluminium carriage plus long-bed forklift.

2001). Therefore when developing and testing 4 different iron-binding resins for pre-separation of trace metals from major abundant earth-alkalines in seawater before injection into the HR-ICP-MS (Kramer and Laan (2003, unpubl. results); see also Beck et al., 2002; Warnken et al., 2000), it was realized these new resins showing optimal separation at low pH  $\sim 1.8$  would also be favorable for FIA-CL as to effectively rule out competition by strong natural organic ligands. Therefore during the 2005 cruise, the most promising resin based on iminodiacetic acid (IDA) functional group was used in combination with FIA-CL, i.e. the following modifications were applied.

Firstly acidification to pH 1.8 was done with 4 mL of threefold quartz distilled  $\text{HNO}_3$  (instead of triple quartz distilled HCl) per L of sample for at least 24 h before analysis on board. Secondly as an additional guarantee for full conversion of Fe(II) to Fe(III) an extra amount of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was added to a final 10  $\mu\text{M}$  concentration in the seawater. Thirdly, instead of previously (2002 cruise) using immobilized 8-hydroxy-quinoline (8HQ), the resin (Toyopearl AF-chelate-650M) was used. This is already derivated with iminodiacetic acid (IDA) by the supplying company. The Fe(III) affinity of IDA has a wider pH range such

that column extraction can be done at the acidified pH  $\sim 1.8$  of the sample, without the need to first bring the pH up to  $\sim 4.5$  by additional reagent ammonium acetate as required for the 8-HQ columns. The IDA comprising two imino-diacetic groups is akin to the NTA chelator comprising three imino-diacetic groups as used by Lohan et al. (2006). Latter authors also report trials by themselves and others showing competition between model dissolved ligands and an 8-HQ column.

## 4. Results

### 4.1. Physical performance in 2002

Throughout the several hydrocasts in 2002 with the Pilot Rosette the success of complete closing of the GO-FLO samplers was about 90–95 % which is at least as good as our past 15 years experiences with single GO-FLO samplers on the 7 mm thin line and triggered by a dropping weight. This confirms the overall reliability of the hydraulics system for tripping samplers to close. Furthermore the smooth vertical profiles of dissolved major nutrients further confirmed that these samplers were not leaking.

#### 4.2. Physical performance in 2005

The complete titanium frame with samplers was handling very well throughout deployment and recovery, even at high wind velocity (Bft. 7) and corresponding rough sea state. Deployment into the water and recovery from the water is similar in time and manpower as for a regular CTD/Rosette requiring two sailors on deck and one winch operator. Pushing the carriage over the deck, and shifting the frame from carriage into the container is best done by three people and takes ca. 3 min. At the normal vertical rates of lowering and uphauling of about  $1 \text{ m s}^{-1}$  the performance was very steady. During one downcast a tilt angle metre had been installed and this had recorded fluctuations of less than  $2^\circ$  angle. This further confirmed the complete system to be very stable during deployment. The success of complete closing of the GO-FLO samplers was better than 85%, the remaining 15% closing problems sometimes due to failing pressure release valves on the GO-FLO, in other instances noticed by deviating nutrient concentrations indicative of leakage after closing (For brandnew GO-FLO samplers occasionally a sharp edge on the ball of ball-valve caused incomplete closing, this is easily remedied by gentle

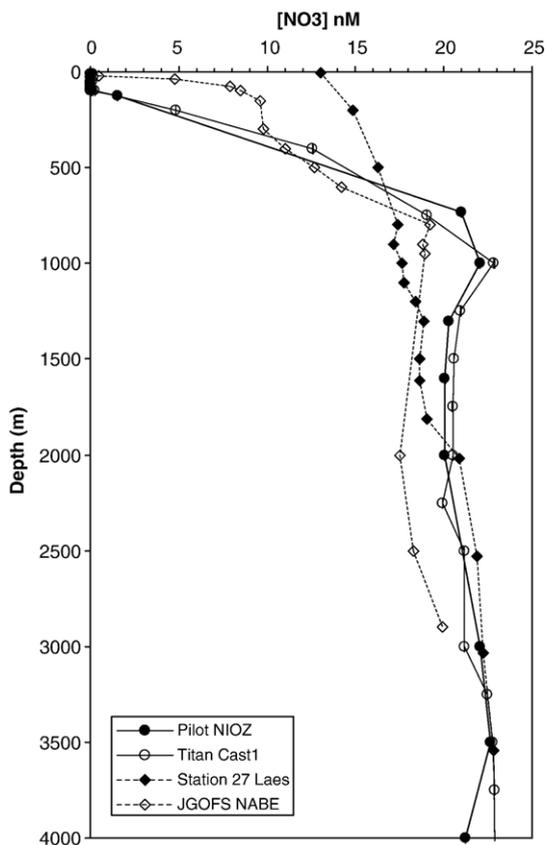


Fig. 7. Vertical profiles of dissolved nitrate at ( $30^\circ \text{N}$ ,  $17.5^\circ \text{W}$ ) in 2002 (filled circles) and 2005 (open circles). Also shown for comparison the nitrate (open diamonds) at ( $47^\circ \text{N}$ ,  $20^\circ \text{W}$ ) after (Martin et al., 1993), and nitrate (filled diamonds) at ( $46^\circ 26' 06'' \text{N}$ ,  $06^\circ 59' 79'' \text{W}$ ) after the station 27 of Laës et al. (2003).

Table 1

Concentrations of dissolved Fe [nM] and dissolved Al [nM] at Station 34, casts 1 and 2 with coated stainless steel pilot frame, cast 3 single GO-FLO samplers at 7 mm hydrowire

Station-cast	Depth	DFe	DAI
Day/Month/Year	[m]	[nM]	[nM]
Latitude, longitude			
Sampling system			
34-1			
24/10/2002	10	0.19	15.2
30.00°N, 17.50°W	25	0.19	15.4
Pilot frame	50	0.29	15.0
	60	0.30	15.2
	70	0.13	13.9
	80	0.09	13.6
	90	0.10	13.6
	100	0.12	13.2
	125	0.15	14.8
	150	0.28	13.3
34-2			
24/10/2002	735	0.49	18.5
30.00°N, 17.50°W	1000	0.48	–
Pilot frame	1300	0.43	24.6
	1600	0.42	23.2
	2000	0.39	18.7
	3000	0.39	21.7
	3500	0.39	21.4
	4000	0.39	–
34-3			
	300	(0.47)*	–
24/10/2002	485	0.40	–
30.00°N, 17.50°W	750	0.50	–
Single GO-FLO's	1700	0.43	–
	2700	0.39	–

\*) Value in brackets is suspect outlier and not plotted in Fig. 8. See Sarthou et al. (2007) for duplicate analyses values of DFe for same samples by IUEM, shown as open symbols in Fig. 8. Kramer et al. (2004) also listed Al values in upper 150 m, but not the deeper values in 735–3500 depth range.

smoothing with a cutting tool). Upon recovery the system, with additional payload of  $\sim 270 \text{ kg}$  of seawater, remained very stable during transportation over the deck with the special carriage, operations were smooth and safe at all ships movements encountered.

Within the laboratory container the temperature was constant and pleasant. There was no laser optics aerosol particles counter available during the cruise, but this will be installed as a permanent monitoring device for future cruises. Thus, apart from the above excellent acceptance test results obtained at shore, we cannot yet report particle densities during at-sea operations.

#### 4.3. Major nutrients in 2002

The deep vertical profile of dissolved nitrate at station 34 casts 1 and 2 is shown by filled circles in Fig. 7. The generally smooth trend of increasing concentrations with depth indicates there was no inadvertent leakage of already closed samplers during the upcast.

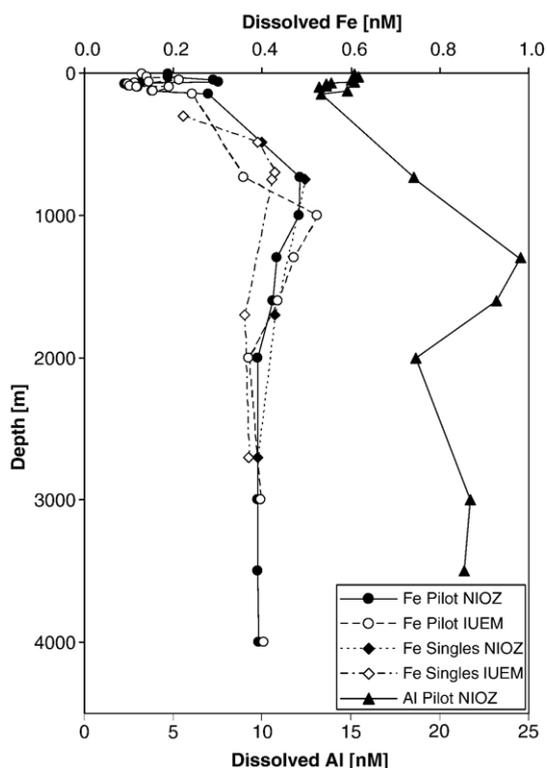


Fig. 8. Vertical profiles of dissolved Fe at (30 °N, 17.5 °W) in 2002 collected with the Pilot Rosette (filled circles for casts 34-1 and 34-2) and the single samplers (filled diamonds for cast 34-3) and analyzed with the NIOZ method. Also shown for the same samples the dissolved Fe as determined by the parallel IUEM method (open symbols). Filled triangles is vertical profile of dissolved Al [nM] at same station 34 in 2002, after Kramer et al. (2004).

#### 4.4. Major nutrients in 2005

The deep vertical profiles of dissolved nitrate at the same (30 °N, 17.5 °W) site as in 2002 shows a similar smooth trend and the 2005 data is in good agreement with the concentrations of the 2002 station occupation (Fig. 7).

#### 4.5. Dissolved Al in 2002

The deep vertical profiles of dissolved Al have previously been shown (Kramer et al., 2004) and here is only given the deep values (Table 1) and profile (Fig. 8) of station 34 (Fig. 8).

#### 4.6. Dissolved Fe in 2002

The deep vertical profile of dissolved Fe (Fig. 8) collected with the Pilot Rosette (station/casts 34-1 and 34-2) is consistent with the smaller dataset of dissolved Fe collected with single samplers (cast 34-3). Moreover the parallel analyses of the same samples with the IUEM method (Sarhou et al., 2007) yields similar results (Fig. 8). Moreover the dissolved Fe concentrations at station 34 are also compatible with several other stations in the

region during the same cruise (not shown, see Sarhou et al., 2007).

#### 4.7. Dissolved Fe in 2005

Two deep vertical profiles collected with the titanium frame system (casts 1 and 2) show excellent agreement among each other (Fig. 9) as well as versus the two deep hydrocasts (3 and 4) obtained with individual mounted bottles (Table 2).

## 5. Discussion

### 5.1. Pilot Rosette versus coated Al frame

The Pilot Rosette as used successfully (Kramer et al., 2003, 2004; Sarhou et al., 2003, 2007) down to 4000 m

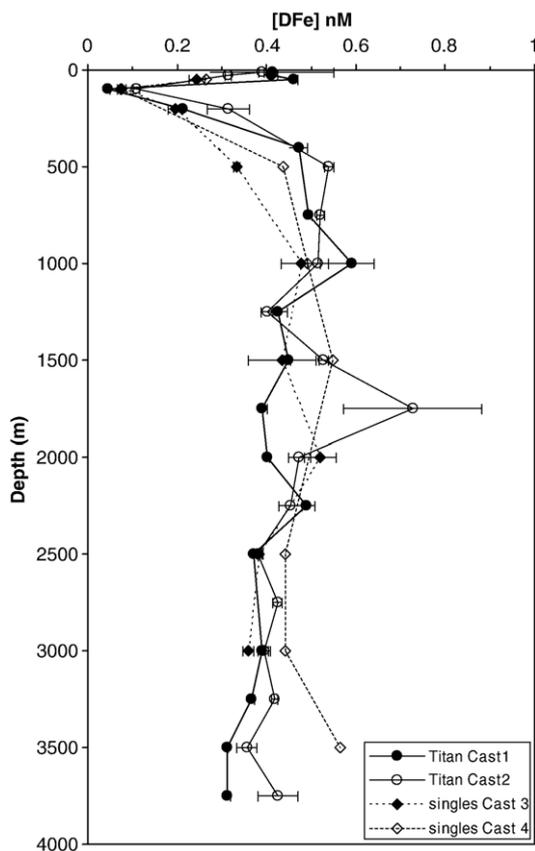


Fig. 9. Dissolved Fe at (30 °N, 17.5 °W) in 2005 collected with the Titan system (Cast 1 filled circles; Cast 2 open circles) and collected with individual samplers (Cast 3 filled diamonds; Cast 4 open diamonds). In Titan Cast 2 the outlier of 0.73 nM at 1750 m has a very high 21% relative standard deviation among the triplicate analyses. However no other anomaly was observed when this sample was analyzed by FIA-CL. Such occasional outlier is reported as per common guidelines (p. 377 of Hunter et al., 2001; pp. 137–138 of De Baar and de Jong, 2001). Yet for further oceanographic/biogeochemical interpretation it is rejected due to poor >10% reproducibility of the triplicate analyses.

Table 2  
Concentrations of dissolved Fe [nM] at Station 6, Expedition 64 PE 241 of R.V. Pelagia

Station-cast	Depth	DFe
Day/Month/Year	[m]	[nM]
Latitude, longitude		
Sampling system		
6–4	10	0.41
05/11/2005	25	0.42
30.00°N 17.5°W	50	0.46
Titan frame	100	0.046
	200	0.21
	400	0.47
	750	0.49
	1000	0.59
	1250	0.43
	1500	0.45
	1750	0.39
	2000	0.40
	2250	0.49
	2500	0.37
	3000	0.39
	3250	0.37
	3500	0.31
	3750	0.31
6–9	10	0.39
07/11/2005	25	0.31
30.00°N 17.50°W		
Titan frame	100	0.11
	200	0.31
	500	0.54
	750	0.52
	1000	0.51
	1250	0.40
	1500	0.53
	1750	(0.73)*
	2000	0.47
	2250	0.45
	2500	0.38
	3000	0.39
	3250	0.42
	3500	0.36
	3750	0.43
6–10	50	0.24
08/11/2005	100	0.076
30.00°N 17.50°W	200	0.20
Single GO-FLO's	500	0.33
	1000	0.48
	1500	0.43
	2000	0.52
	2500	0.38
	3000	0.36
6–12	50	0.27
08/11/2005	100	0.074
30.00°N 17.50°W		
Single GO-FLO's	500	0.44
	1000	0.49
	1500	0.55
	2500	0.44

Table 2 (continued)

Station-cast	Depth	DFe
Day/Month/Year	[m]	[nM]
Latitude, longitude		
Sampling system		
Single GO-FLO's	3000	0.44
	3500	0.56

Casts 4 and 9 with titanium frame, casts 10 and 12 with single GO-FLO samplers. \*) Value in brackets is suspect outlier but is plotted in Fig. 9.

depth during the IRONAGES III cruise in October 2002 is similar to a powder-coated aluminium Rosette frame carrying 12 GO-FLO samplers used more recently during a CLIVAR A16 cruise track in the northeast Atlantic Ocean in the 19 May–11 August 2003 period, where it was deployed to 1000 m depth with 0.38 inch four-conductor, polyurethane-coated Kevlar line (Landing et al., 2004, 2006). Latter type frame has also been used successfully during the 2004 SAFe cruise in the North Pacific (Johnson et al., 2005, 2007) and Pacific section cruises (Brown et al., 2006; Hansard et al., 2006; Hiscock et al., 2006). There has been some concern about the Zn-anode in this type frame, and suggestions have been made to replace this with a Mg anode (Cutter et al., 2006). Aluminium having an electrode potential close to zinc, would require considerable dissolution of the sacrificial Zn-anode, and even more of a Mg-anode. Titanium or special SS-316 stainless steel do not need such protective anode in seawater.

## 5.2. General performance Titan system

The new titanium-frame system greatly improves the overall efficiency of expeditions. Firstly one hydrocast takes the about 3–4 hours as common practice for regular CTD/Rosettes, to yield 24 sampling depths. In comparison the same 24 sampling depths done by 3 hydrocasts of 8 individual samplers mounted on the hydrowire takes much more time, more than threefold as the mounting of each sampler, the dropping of the trip-weight, and the dismounting upon recovery typically take an extra 1 hour for an experienced team of 3 scientists. Thus overall shiptime expenditure for 24 depths used to be about 12–15 hours, fourfold slower than with the new titanium frame. With GEOTRACES aiming for complete ocean sections of closely spaced deep stations this fourfold gain is immense, corresponding to a fourfold gain in shiptime efficiency. Typical costs of the shiptime alone (crew salary, food, fuel) are in the order of Euro ca. € 10,000 – to ca. € 40,000 – per day from a smaller vessel to a very large icebreaker.

Moreover the handling requires far less manpower, notably for (dis-)mounting and hand-carrying single samplers over the ship to and from the clean laboratory container. The filtrations with cartridges also go routinely and efficiently. Thus per shipboard scientist there is far more time available for final shipboard analyses with FIA or otherwise, this furthermore improving the overall efficiency of sample throughput.

Alternatively for the same configuration a strictly mechanical system (trip-wires led to a central 24 position release unit) is not unconceivable. However we already had used the Multivalve (Ober et al., 2002) for many years in our regular CTD/Rosette systems. Moreover, in the development of the Ti frame, our various adjustments in relative positioning of GO-FLO samplers and central Multivalve are easier with the flexible silicone tubing than with mechanical wires which require very exact length adjustments. Moreover in our new prototype sampling bottles the hydraulics is an integral part of their design, rather than the here described attachment pistons (Fig. 4a) to each GO-FLO sampler.

Last but not least we reckon the overall system and procedure is far less prone to random inadvertent contamination, i.e. the overall analytical reliability of the dataset would be improved. This however will only be confirmed during the upcoming large section cruises in the 2007–2008 International Polar Year and beyond when indeed large datasets are envisioned. Nevertheless the results thus far for dissolved Fe and Al, as discussed below, are as good as those obtained with the single samplers, the latter both in this study and in the published literature.

### 5.3. Dissolved Al

The profile is alike previously published profiles (Hydes, 1983; Measures, 1995), but less pronounced, as our station 34 and many other stations (see Kramer et al., 2004) were taken at a much larger distance from the Strait of Gibraltar. Nearby stations (30N, 23.37W; 29N, 23.94W; 28N, 24.50W) of the 2003 CLIVAR A16 section (Landing et al., 2004) are situated in the northwestern part of the region studied by Kramer et al. (2004). The dissolved Al at latter 2003 CLIVAR A16 stations (0–1000 m; see page 9 of Geotraces 2006) appears to be in the same 9–16 nM range found in the upper 200 m at our station 34 and at other stations of Kramer et al. (2004). The CLIVAR A16 data in upper 1000m also tends to confirm the distinct north–south gradients observed in the upper 150 m (Fig. 6 of Kramer et al., 2004). Upon publication of the CLIVAR A16 dataset a more detailed comparison can be made.

### 5.4. Dissolved Fe

Comparison of one of the Titan casts in 2005 with the Pilot Rosette in 2002 shows excellent agreement (Fig. 10). This in combination with the consistency versus single samplers (Figs. 8, 9) as well as with independent analyses of samples of 2002 by the IUEM (Fig. 8) tends to support reliability of the overall sampling and filtration system for obtaining clean samples to measure dissolved Fe in seawater.

The generally somewhat higher values of NIOZ versus IUEM is akin to a previous study by the same research groups (Bowie et al., 2003; then UBO is now IUEM). Moreover in the recent SAFe intercomparison, again the IUEM values were in good agreement with, and again somewhat lower than, the NIOZ values. This and other findings (Bowie et al., 2003, 2006; Johnson et al., 2007) tend to suggest that, the clean sampling and filtration now having been improved so much, now the overall accuracy of the final analytical method has become the most critical step in the overall procedure. Here the chemiluminescence method after Obata et al. (1993) obviously is very powerful as a reliable shipboard method with fine *reproducibility* (De Jong et al., 1998; Bowie et al., 2003, 2006; Sarthou et al., 2007). Similarly the Flow Injection method using spectrophotometry for final detection (Measures et al., 1995) has been proven very powerful (e.g. Lohan et al., 2006). Yet now facing the next stage of pursuing worldwide *accuracy* between various laboratories and datasets, further refinements of these methods towards improved intrinsic *accuracy* need to be tinkered upon.

At our station the dissolved Fe tends to increase from typically about 0.1–0.2 nM in the upper waters to maximum values of about 0.4 to 0.5 nM in the 700–1200 m depth range, then remains quite constant (or slightly decreases) at about 0.4 nM quite uniformly in the deep 2000–4000 m waters (Figs. 8–10). For an E–W transect (23.6 to 45 °W) along ca. 30 °N similar values of 0.37 to 0.60 nM were reported for six surface water samples (Bergquist and Boyle, 2006). For two vertical profiles collected in the upper 197 m (summer) and 1050 m (winter) at 30 °N, 45 °W the dissolved Fe was reported in a similar range of 0.36 to 0.68 nM, excluding two outliers (Bergquist and Boyle, 2006). Please notice the 0.4 µm nominal size cutoff for filtered seawater of Bergquist and Boyle (2006) versus the 0.2 µm used here; in combination with other factors (filtration speed and period; particle size spectrum, etc.) this may, or may not, yield an offset between the independent datasets. More towards (10 °N) and at (0 °N) the equator, dissolved Fe values in the ca. 0.15 to 1.5 nM range have been reported in the upper 200 m along an east–west transect, where the

higher values were attributed to recent aeolian dust input (Croot et al., 2004a,b). Indeed at 10 °N, 45 °W such higher values ranging from 0.37 to 1.19 nM have also been reported for two vertical profiles in the upper 200 m (summer) and 3400 m (winter) of the tropical Atlantic Ocean (Bergquist and Boyle, 2006).

The dissolved Fe is comparable with the JGOFS-NABE station (47°N, 20°W) of Martin et al., 1993) which had been analyzed by the excellent classical solvent extraction/GFAAS method (Bruland et al., 1979). Slight deviations such as higher values at about 500m and lower values at 2000–3000 m versus JGOFS NABE are to be expected due to different locations and hydrography. For example the dissolved nitrate in deep waters at our station tends to be higher than at JGOFS-NABE (Fig. 7), consistent with the general southward increase of deep nutrients in the Atlantic basin (GEOSECS, 1981). Seasonality (springtime of JGOFS-NABE and autumn at our station) of wind mixed layer depth and biological uptake/regeneration also plays a role in the surface waters (Figs. 7, 10).

The IRONAGES-2 cruise station 27 (~47 °N, ~07 °W) of Laës et al. (2003) was collected in late winter (March 2002) in the Gulf of Biscay, i.e. much closer to the continental shelf and slope off France and the Iberian Peninsula. The severe winter mixing yields higher dissolved nitrate in the upper ~500 m than at the stratified JGOFS NABE site at same latitude in the later spring bloom season, or the more permanent stratification at our more southerly station in the Canary basin (Fig. 7). The generally higher dissolved Fe in the upper ~800 m of the Station 27 is consistent with such seasonality, while at about 1000 m depth the dissolved Fe values of all stations (Fig. 10) tend to be closer at about 0.5–0.7 nM. At greater depths the Station 27 shows a strong increase to concentrations exceeding 1 nM consistent with the continental slope as an Fe source (Laës et al., 2003).

Within the more western Sargasso Sea, winter values in surface waters have been found to decrease from 0.8 nM at 26 °N to 0.2 nM at 31 °N (Wu and Boyle, 2002; not shown). In the subsurface waters the dissolved Fe also was reported to show an increasing trend from about 0.2 nM at 200 m depth to quite uniform 0.6 nM at depths below 1000 m (Wu and Boyle, 2002; not shown).

Far more southerly (44°S, 20°E; 47°S, 20°E; 49–50°S, 20°E; 60°S, 20°E) the deep (>2000 m) dissolved Fe tends to be lower again in the 0.3 to 0.4 nM range (not shown; De Jong et al., 1999; in Table A1. of De Baar and de Jong, 2001). This is consistent with deep values of ca. 0.4 nM reported for deep waters of Antarctic origin in the South Atlantic (Bergquist and Boyle, 2006).

Finally some stations (32°N, 22.25°W; 30°N, 23.37°W; 29°N, 23.94°W; 28°N, 24.50°W) of the 2003 CLIVAR A16 section (Landing et al., 2004) are situated in the northwestern part of our study region (Sarhou et al., 2003, 2007; this work). The dissolved Fe at latter 2003 CLIVAR A16 stations (0–1000 m; see page 9 of Geotraces 2006) appears to show a similar increasing trend with depth (not shown). At greater depths (~500–1000 m) some higher values (Fe >0.75 nM, some Fe > 1 nM) perhaps resemble the significantly higher dissolved Fe (maximum of 0.64 at 1300 m) of the other deep station 10 (31.71°N 22.00°W) in our region (Sarhou et al., 2007) as compared to the deep station (30 °N, 17.5 °W) here reported and all other stations in the region (Sarhou et al., 2003, 2007). Upon publication

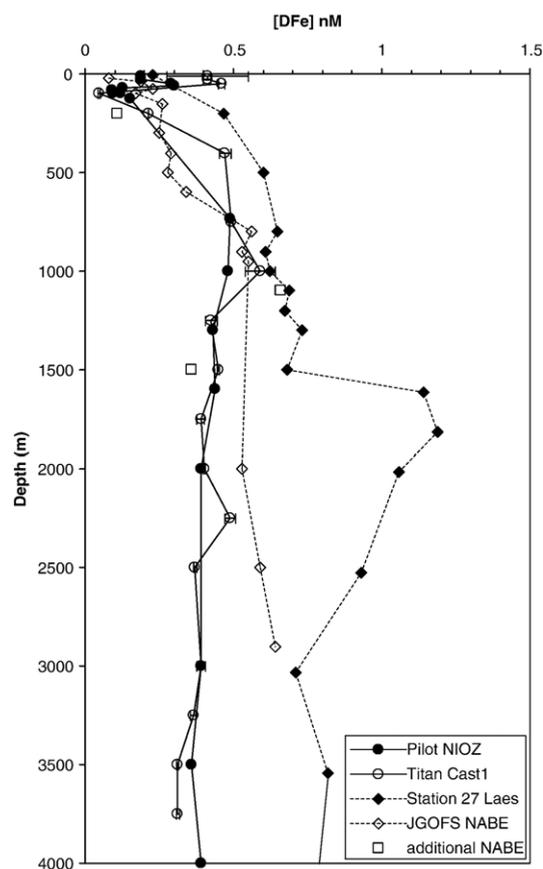


Fig. 10. Comparison of vertical profiles in 2002 by Pilot Rosette (filled circles) and in 2005 by Titan system (open circles). Also shown dissolved Fe (filled diamonds) at (46°26′06′ N, 06°59′79′ W) after IRONAGES-2 cruise station 27 of Laës et al. (2003), and dissolved Fe (open diamonds) at (47 °N, 20 °W) after (Martin et al., 1993) including 3 additional datapoints (open squares) after Laës et al. (2003). Notice in latter profiles (Laës et al., 2003; Martin et al., 1993) the maxima at about 1000–2000 m depth which have been ascribed to Labrador Sea Water having contacted the shelf and slope (Laës et al., 2003). Fig. 7 shows nitrate of the same stations.

of the CLIVAR A16 dataset a more detailed comparison can be made.

The above discussed range and seasonality of surface water concentrations, and the mentioned about 0.3 to 1.2 nM range in subsurface waters, will require the intended deep ocean sections of the GEOTRACES program to confirm accuracy of the here discussed data. Moreover only such larger dataset will allow, by observing trends in time and space, to deduce the causes for the distribution of dissolved Fe in the oceans.

## 6. Conclusions and recommendations

The new Titan system (Kevlar hydrowire plus titanium sampling frame plus clean-air laboratory van) has been proven to yield excellent reliable results for dissolved Fe in seawater at a deep station in 2005 in the Canary Basin. These results are compatible with previous findings at the same station in 2002, as well as other dissolved Fe data from the published literature in the same region. Moreover the dissolved Al collected and analyzed in 2002 with the Pilot System is consistent with dissolved Al data in the published literature.

The system constitutes an about fourfold reduction of required shiptime for sample collection, thus allowing large scale sampling efforts of deep profiles along ocean sections. Moreover the shipboard time required for handling and filtration per sample is decreased, thus allowing more time to be dedicated to shipboard analyses.

Ever since the pioneering major step forward by Bruland et al. (1979) the teflon-coated GO-FLO sampler (General Oceanics Inc.) has been the pivotal sampler of choice during more than 25 years investigation of trace elements in the oceans. However a teflon-coating is required in order to separate the PVC (which contains many contaminants) from the seawater sample. Even then the bottles are not appropriate for some elements (e.g. Sn, a major component of PVC stabilizer; Cutter et al., 2006). Also the metal parts are of a stainless steel alloy which has been observed to develop corrosion by seawater. Meanwhile new type plastics have come on the market, and are used at large scale in the food- and beverages industry as well as pharmaceutical industry, where inadvertent contamination also is to be avoided. We have built two prototypes of a novel design sampler for the 21st century of high-purity plastic (food-industry certified), where the few inevitable metal parts are of titanium.

Finally, further refinements towards improved accuracy of the very powerful shipboard methods after Obata et al. (1993) or Measures et al. (1995), or other shipboard analytical methods as well, are required to

arrive at acceptable accuracy (for example better than 5%) between worldwide laboratories and their datasets.

### 6.1. Note added in proof

A second titanium frame with set of 24 new GO-FLO samplers was tested successfully for dissolved Fe and Al in April 2007 in the deep Northeast Atlantic Ocean. Moreover two new prototype water samplers were successfully tested, and sensible deep Fe and Al values were obtained. Results of this April 2007 test cruise will be reported in due course.

## Acknowledgements

All authors are much indebted to the master, officers and crew of our research vessel Pelagia for their joyful support during cruises IRONAGES-3 and 64 PE 241. This research was supported by the IRONAGES program (Iron Resources and Oceanic Nutrients; Advancements of Global Environmental Simulations) of the European Union Fifth Framework Program under contract number EVK2-CT1999-00031, the Marine Research Facilities of The Netherlands, and the second Netherlands-Bremen Oceanography program NEBROC-2. The designs of here described Titan and Multivalve systems are property of Royal NIOZ. Constructive comments of two referees are much appreciated and have led to major improvements of the manuscript, notably of the historical context of the introduction. Special thanks are to Dr. J. Nishioka and Prof. H. Obata for personal communications on the Ti armored hydrowire aboard two vessels of Japan, and to Dr. M.J.A. Rijkenberg and Prof. P.J. Statham for personal communications on the two titanium frames existing and in use in Britain.

The authors are grateful for the kind invitation to submit a manuscript for this special issue in honor of Dr. Peter Brewer. The lead author (HdB) is most grateful to Dr. Peter Brewer for his inspiration and support during an exciting PhD thesis period 1978–1983 upon his invitation at Woods Hole, and for the enduring friendship ever since. Professionally and privately those were very happy years for both of us and our families. Moreover those were the romantic days when large parts of the Periodic Table were undiscovered territory within the oceans, the hunting grounds of senior or contemporary PhD students. Some succeeded to be first and famous, others were by-passed and got second with lesser glory; but that is merely vanity, after all even our common hero Claire Patterson has virtually been forgotten (Bryson, 2004). Similarly the introduction of this article is by no means an exhaustive overview of historic developments, instead it merely

serves as a brief description of some major steps between the first pioneering work of Peter Brewer and the here described new Titan sampling system.

At the time Peter Brewer got more and more involved in the role of the oceans in the global carbon cycle, notably the uptake of carbon dioxide from the atmosphere in the oceans. Nowadays Peter's contributions to latter line of research on the major element carbon in the sea are well known and appreciated. This manuscript is dedicated to his pioneering and stimulating role in the 1960–1980 era on the trace elements in sea water.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.marchem.2007.07.009](https://doi.org/10.1016/j.marchem.2007.07.009).

## References

- Amakawa, H., Nozaki, Y., Alibo, D.S., Zhang, J., Fukugawa, K., Nagai, H., 2004. Neodymium isotopic variations in Northwest Pacific waters. *Geochimica et Cosmochimica Acta* 68 (4), 715–727.
- Bacon, M.P., Edmond, J.M., 1972. Barium at Geosecs III in the southwest Pacific. *Earth and Planetary Science Letters* 16, 66–74.
- Beck, N.G., Franks, R.P., Bruland, K.W., 2002. Analysis for Cd, Cu, Ni, Zn and Mn in estuarine water by inductively coupled plasma mass spectrometry coupled with an automated flow injection system. *Analytica Chimica Acta* 455, 11–22.
- Bell, J., Betts, J., Boyle, E., 2002. MITESS: a moored in situ trace element serial sampler for deep-sea moorings. *Deep-Sea Research* 49, 2103–2118.
- Bender, M.L., Snead, T., Cahn, L.H., Bacon, M.P., Edmond, J.M., 1972. Barium intercalibration at Geosecs I and III. *Earth and Planetary Science Letters* 16, 81–83.
- Bender, M.L., Klinkhammer, G., Spencer, D.W., 1977. Manganese in seawater and the marine manganese balance. *Deep-Sea Research* 24, 799–812.
- Bergquist, B.A., Boyle, E.A., 2006. Dissolved iron in the tropical and subtropical Atlantic Ocean. *Global Biogeochemical Cycles* 20 (3), GB1015. [doi:10.1029/2005GB002505](https://doi.org/10.1029/2005GB002505).
- Bowie, A.R., Achterberg, E.P., Mantoura, R.F.C., Worsfold, P.J., 1998. Determination of subnanomolar levels of iron in seawater using flow injection with chemiluminescence detection. *Analytica Chimica Acta* 361, 189–200.
- Bowie, A.R., Achterberg, E.P., Blain, S., Boye, M., Croot, P.L., de Baar, H.J.W., Laan, P., Sarthou, G., Worsfold, P.J., 2003. Shipboard intercomparison of dissolved iron in surface waters along a north–south transect of the Atlantic Ocean. *Marine Chemistry* 84, 19–34.
- Bowie, A., Achterberg, E., Croot, P., de Baar, H., Laan, P., Moffett, J., Ussher, S., Worsfold, P., 2006. A community-wide intercomparison exercise for determination of dissolved iron in seawater. *Marine Chemistry* 98, 81–99.
- Boyle, E., Edmond, J.M., 1975. Copper in surface waters south of New Zealand. *Nature* 253, 107–109.
- Boyle, E.A., Sclater, F.R., Edmond, J.M., 1977. The distribution of dissolved copper in the Pacific. *Earth and Planetary Science Letters* 37, 38–54.
- Boyle, E.A., Sclater, F.R., Edmond, J.M., 1976. On the marine geochemistry of cadmium. *Nature* 263, 42–44.
- Boyle, E.A., Bergquist, B.A., Kayser, R., Mahowald, N., 2005. Iron, manganese, and lead at Hawaii Ocean Time-series station ALOHA: temporal variability and an intermediate water hydrothermal plume. *Geochimica et Cosmochimica Acta* 69, 933–952.
- Brewer, P.G., 1975. Minor elements in seawater. In: Riley, J.P., Skirrow, G. (Eds.), Second edition. *Chemical Oceanography*, vol. I. Academic Press, pp. 415–496. Chapter 7.
- Brewer, P.G., Riley, J.P., Culkin, F., 1965. The chemical composition of the hot salty water from the bottom of the Red Sea. *Nature* 206, 1345–1346.
- Brewer, P.G., Spencer, D.W., Robertson, D.E., 1972. Trace element profiles from the GEOSECS II test station in the Sargasso Sea. *Earth and Planetary Science Letters* 16, 111–116.
- Brown, M.T., Measures, C.I., Landing, W.F., Buck, C.S., 2006. Trace element distributions along p16s show the effect of Australian Continental dust inputs. Abstract OS21C-1607 at AGU Fall Meeting, San Francisco.
- Bruland, K.W., 1980. Oceanographic distributions of cadmium, zinc, nickel and cadmium in the north Pacific. *Earth and Planetary Science Letters* 47, 176–198.
- Bruland, K.W., 1983. Trace elements in sea-water. In: Riley, J.P., Chester, R. (Eds.), *Chemical Oceanography*, vol. 8. Academic Press, London, pp. 157–221. Chapter 45.
- Bruland, K.W., Rue, E.L., 2001. Analytical methods for the determination of concentrations and speciation of iron. In: Turner, D.R., Hunter, K.A. (Eds.), *Biogeochemistry of Fe in Seawater*. SCOR-IUPAC series. J Wiley, Baltimore, pp. 255–289. Chapter 6.
- Bruland, K.W., Knauer, G.A., Martin, J.H., 1978. Zinc in northeast Pacific waters. *Nature* 271, 741–743.
- Bruland, K.W., Franks, R., Knauer, G.A., Martin, J.H., 1979. Sampling and analytical methods for the determination of copper, cadmium, zinc and nickel at the nanogram per liter level in sea water. *Analytica Chimica Acta* 105, 233–245.
- Bryson, B., 2004. Getting the lead out, A Short History of Nearly Everything, Black Swan edition., pp. 193–205. Chapter 10.
- Campbell, J.A., 1983. The geochemical ocean sections study—GEOSECS. In: Riley, J.P., Chester, R. (Eds.), *Chemical Oceanography*, vol. 8. Academic Press, London, pp. 89–155. Chapter 44.
- CEN, 2002. Particulate air filters for general ventilation — determination of the filtration performance. European Committee for Standardization, Technical Committee 195, Work Group 1, Report EN 779:2002. <http://www.cen.eu/cenorm/>.
- Chan, L.H., Drummond, D., Edmond, J.M., Grant, B., 1977. On the barium data from the Atlantic GEOSECS expedition. *Deep-Sea Research* 24, 613–649.
- Chase, Z., Paytan, A., Johnson, K.S., Street, J., Chen, Y., 2006. Input and cycling of iron in the Gulf of Aqaba, Red Sea. *Global Biogeochemical Cycles* 20 (3), GB3017. [doi:10.1029/2005GB002646](https://doi.org/10.1029/2005GB002646).
- Coale, K.H., Worsfold, P., de Baar, H., 1999. Iron age in oceanography. *Eos, Transactions of the American Geophysical Union* 80, 337–382.
- Croot, P.L., Andersson, K., Ozturk, M., Turner, D.R., 2004a. The distribution and speciation of iron along 6°E in the Southern Ocean. *Deep-Sea Research*. Part 1. *Oceanographic Research Papers* 51 (22–24), 2857–2879.
- Croot, P.L., Streu, P., Baker, A.R., 2004b. Short residence time for iron in surface seawater impacted by atmospheric dry deposition from Saharan dust events. *Geophysical Research Letters* 31, L23S08. [doi:10.1029/2004GL020153](https://doi.org/10.1029/2004GL020153).
- Cutter, G., Andersson, P., Boyle, E., Francois, R., Jeandel, C., Masque, P., Obata, H., Rutgers van der Loeff, M., Zhong, S., 2006.

- Geotraces Intercalibration Planning Document. 18 pp., Downloadable pdf at: <http://www.geotraces.org/> or at: <http://www.ideo.columbia.edu/res/pi/geotraces/>.
- Danielsson, L.-G., Magnusson, B., Westerlund, S., 1978. An improved metal extraction procedure for the determination of trace metals in sea water by atomic absorption spectrometry with electrothermal atomisation. *Analytica Chimica Acta* 98, 47–57.
- De Baar, H.J.W., 1994. von Liebig's Law of the minimum and plankton ecology (1899–1991). *Progress in Oceanography* 33, 347–386.
- De Baar, H.J.W., de Jong, J.T.M., 2001. Distributions, sources and sinks of iron in seawater. In: Turner, D.R., Hunter, K.A. (Eds.), *Biogeochemistry of Fe in Seawater*. SCOR-IUPAC series. J Wiley, Baltimore, pp. 123–253. Chapter 5.
- De Baar, H.J.W., La Roche, J., 2003. Metals in the oceans; evolution, biology and global change. In: Lamy, F., Wefer, G. (Eds.), *Marine Scientific Frontiers for Europe*. Springer Verlag, Berlin, pp. 79–105.
- De Baar, H.J.W., Bacon, M.P., Brewer, P.G., 1983. Rare earth distributions with a positive cerium anomaly in the western North Atlantic Ocean. *Nature* 301, 324–327.
- De Baar, H.J.W., Bacon, M.P., Brewer, P.G., Bruland, K.W., 1985. Rare earth elements in the Atlantic and Pacific Oceans. *Geochimica et Cosmochimica Acta* 49, 1943–1959.
- De Baar, H.J.W., Buma, A.G.J., Nolting, R.F., Cadée, G.C., Jacques, G., Tréguer, P.J., 1990. On iron limitation of the Southern Ocean: experimental observations in the Weddell and Scotia Seas. *Marine Ecology. Progress Series* 65, 105–122.
- De Baar, H.J.W., de Jong, J.T.M., Nolting, R.F., van Leeuwe, M.A., Timmermans, K.R., Templin, M., Rutgers van der Loeff, M.M., Sildam, J., 1999. Low dissolved Fe and the absence of diatom blooms in remote Pacific waters of the Southern Ocean. *Marine Chemistry* 66, 1–34.
- De Jong, J.T.M., Den Das, J., Bathmann, U., Stoll, M.H.C., Kattner, G., Nolting, R.F., de Baar, H.J.W., 1998. Dissolved iron at subnanomolar levels in the Southern Ocean as determined by shipboard analysis. *Analytica Chimica Acta* 377 (2–3), 113–124.
- De Jong, J.T.M., Croot, P.L., De Baar, H.J.W., 1999. Distribution of iron in the surface and deep waters of the Southern Ocean along 20 °E. Abstract in: *Eos, Trans. Am. Geophys. Union*, vol. 80(49), p. 161.
- De Jong, J.T.M., Boye, M., Schoemann, V.F., Nolting, R.F., de Baar, H.J.W., 2000. Shipboard techniques based on flow injection analysis for measuring dissolved Fe, Mn and Al in seawater. *Journal of Environmental Monitoring, Royal Society of Chemistry* 2, 496–502.
- Elderfield, H., Greaves, M., 1982. The rare earth elements in seawater. *Nature* 296, 214–219.
- Freimann, P., Schmidt, D., Schomaker, K., 1983. Mercos — a simple teflon sampler for ultratrace metal analysis in sea-water. *Marine Chemistry* 14, 43–48.
- GEOSecs Atlantic Expedition (1981). NSF, Washington DC, US Government Printing Office; Volume 1, Hydrographic Data, US Govt. Pr.Off. Stock Number 038-000-00491-3, xxix+ 121 pp.; Volume 2, Sections and Profiles, US Govt. Pr.Off. Stock Number 038-000-00435-1, xiv+ 198 pp.
- GEOTRACES Planning Group, 2006. GEOTRACES Science Plan. Baltimore, Maryland: Scientific Committee on Oceanic Research. 87 pp. Downloadable pdf at: <http://www.geotraces.org/>.
- Gerringa, L.J.A., Veldhuis, M.J.W., Timmermans, K.R., Sarthou, G., De Baar, H.J.W., 2006. Co-variance of dissolved Fe-binding ligands with phytoplankton characteristics in the Canary Basin. *Marine Chemistry* 102, 276–290.
- Gordon, R.M., Martin, J.H., Knauer, G.A., 1982. Iron in northeast Pacific waters. *Nature* 299, 611–612.
- Grasshoff, K., 1983. Automated chemical analysis. In: Grasshoff, K., Ernhardt, M., Kremling, K. (Eds.), *Methods of seawater analysis*. Verlag, pp. 263–289.
- Gregg, W., Ginoux, P., Schopf, P., Casey, N., 2003. Phytoplankton and iron: validation of a global three-dimensional ocean biogeochemical model. *Deep-Sea Research. Part 2. Topical Studies in Oceanography* 50, 3143–3169.
- Hansard, S.P., Landing, W.F., Measures, C.I., 2006. Dissolved Fe(II) in the Pacific Ocean: measurements from the P16N CLIVAR/CO2 repeat hydrography cruise. Abstract OS21C-1605 at AGU Fall Meeting, San Francisco.
- Haraldsson, C., Westerlund, S., 1988. Trace metals in the water column of the Black Sea and Framvaren Fjord. *Marine Chemistry* 23, 417–424.
- Hiscock, W.T., Measures, C.I., Landing, W.F., Buck, C., 2006. Input and transport processes revealed in trace metal distributions along P16N. Abstract OS21C-1606 at AGU Fall Meeting, San Francisco.
- Hunter, K.A., Boyd, P.W., Bruland, K.W., Buffle, J., Buat-Ménard, P., de Baar, H.J.W., Duce, R.A., Sunda, W.J., Jickells, T.D., Moffett, J.W., Rue, E.L., Spokes, L.J., Sulzberger, B., Turner, D.R., Waite, T.D., Watson, A.J., Whitfield, M., 2001. Summary and recommendations. In: Turner, D., Hunter, K.A. (Eds.), *Biogeochemistry of Iron in Seawater*. IUPAC Book Series on Analytical and Physical Chemistry of Environmental Systems, vol. 7. John Wiley and Sons Ltd, pp. 373–387. Chapter 9.
- Hydes, D.J., 1979. Aluminium in seawater; control by inorganic processes. *Science* 205, 1260–1262.
- Hydes, D.J., 1983. Distribution of Al in waters of the North East Atlantic 25 degr. N to 35 degr. N. *Geochimica et Cosmochimica Acta* 47, 967–973.
- Johnson, K.S., et al., 2003. Surface ocean-lower atmosphere interactions in the Northeast Pacific Ocean gyre: aerosols, iron and the ecosystem response. *Global Biogeochemical Cycles* 17, 32–42.
- Johnson, K., Boyle, E., Bruland, K., Coale, K., Measures, C., Moffett, J., 2005. Sampling and analysis of Fe: the SAFE iron intercomparison cruise. Abstract at February 2006 AGU/ASLO Ocean Sciences, *Eos Trans. AGU. Ocean Sci. Meet. Suppl.*, vol. 87(36). Abstract OS11N-02, 2005.
- Johnson, K.S., et al., 2007. Developing standards for dissolved iron in seawater. *Eos, Transactions of the American Geophysical Union* 88 (11), 131–132.
- Kinrade, J.D., van Loon, J.C., 1974. Solvent extraction for use with flame atomic absorption spectrometry. *Analytical Chemistry* 46, 1894–1898.
- Kramer, J., Laan, P., van Ooijen, J.C., Sarthou, G., Timmermans, K.R., de Baar, H.J.W., 2003. Distribution of aluminium in the subtropical waters of the North Atlantic Ocean, EGU/AGU; Joint Assembly, OS12, Nice, France.
- Kramer, J., Laan, P., Sarthou, G., Timmermans, K.R., de Baar, H.J.W., 2004. Distribution of aluminium in the high atmospheric input region of the subtropical waters of the North Atlantic Ocean. *Marine Chemistry* 88 (3–4), 85–101.
- Laës, A., Blain, S., Laan, P., Achterberg, E.P., Sarthou, G., de Baar, H.J.W., 2003. Deep dissolved iron profiles in the eastern North Atlantic in relation to water masses. *Geophysical Research Letters* 30 (17), 1902. doi:10.1029/2003GL017902.
- Laës, A., Blain, S., Laan, P., Ussher, S.J., Achterberg, E.P., Tréguer, P., de Baar, H.J.W., 2007. Sources and transport of dissolved iron and manganese along the continental margin of the Bay of Biscay. *Biogeosciences* 4, 181–194.
- Landing, W.M., 1983. The biogeochemistry of manganese and iron in the Pacific Ocean, PhD Thesis, University of California at Santa Cruz, 202 pp.

- Landing, W.M., Bruland, K.W., 1981. The vertical distribution of iron in the northeast Pacific. Abstract in: *Eos, Transactions AGU*, vol. 62, p. 906.
- Landing, W.M., Bruland, K.W., 1987. The contrasting biogeochemistry of iron and manganese in the Pacific Ocean. *Geochimica et Cosmochimica Acta* 51, 29–43.
- Landing, W.M., Cutter, G.A., Dalziel, J.A., Flegal, A.R., Schmidt, D., Shiller, A., Statham, P., Westerlund, S., Resing, J., 1995. Analytical intercomparison results from the 1990 Intergovernmental Oceanographic Commission open-ocean baseline survey for trace metals: Atlantic Ocean. *Marine Chemistry* 49, 253–265.
- Landing, W.M., Measures, C.I., Buck, C.S., Brown, M., 2004. Sections of dissolved iron and aluminum from the 2003 repeat hydrography A16N expedition. Abstract at February 2004 AGU/ASLO Ocean Sciences, *Eos Trans. AGU. Ocean Sci. Meet. Suppl.*, vol. 84(52). Abstract OS31L-07.
- Landing, W.M., Measures, C., Resing, J., 2006. Ocean sections of dissolved Fe, Ni, Cu, Zn, Cd, and Pb. Abstract OS16M-22 at February 2006 AGU/ASLO Ocean Sciences, *Eos Trans. AGU. Ocean Sci. Meet. Supplement*, vol. 87(36). See also Landing, W.F., Buck, C.S., Bizimis, M., Measures, C.I., Abstract OS34B-03 at AGU Fall Meeting, San Francisco.
- Lewis, B.L., Landing, W.M., 1991. The biogeochemistry of manganese and iron in the Black Sea. *Deep-Sea Research. Part 2. Topical Studies in Oceanography* 38, 773–803.
- Lohan, M.C., Aguilar-Islas, A.M., Bruland, K.W., 2006. Direct determination of iron in acidified (pH 1.7) seawater samples by flow injection analysis with catalytic spectrophotometric detection: application and intercomparison. *Limnology and Oceanography Methods* 4, 164–171.
- Martin, J.H., Fitzwater, S.E., 1988. Iron deficiency limits phytoplankton growth in the northeast Pacific subarctic. *Nature* 331, 341–343.
- Martin, J.H., Fitzwater, S.E., Gordon, R.M., Hunter, C.N., Tanner, S.J., 1993. Iron, primary production and carbon–nitrogen flux studies during the JGOFS North Atlantic Bloom Experiment. *Deep-Sea Research. Part 2. Topical Studies in Oceanography* 40, 115–134.
- Measures, C.I., 1995. The distribution of Al in the IOC stations of the Eastern Atlantic between 30-degrees-S and 34-degrees-N. *Marine Chemistry* 49 (4), 267–281.
- Measures, C.I., Yuan, J., Resing, J.A., 1995. Determination of iron in seawater by flow injection analysis using in-line preconcentration and spectrophotometric detection. *Marine Chemistry* 50, 3–12.
- Moody, J.R., Lindstrom, R.M., 1977. Selection and cleaning of plastic containers for storage of trace-element samples. *Analytical Chemistry* 49 (14), 2264–2267.
- Nédélec, F., Statham, P.J., Mowlem, M., 2007. Processes influencing dissolved iron distributions below the surface at the Atlantic Ocean–Celtic Sea shelf edge. *Marine Chemistry* 104, 156–170.
- Obata, H., Karatani, H., Nakayama, E., 1993. Automated determination of iron in seawater by chelating resin concentration and chemiluminescence. *Analytical Chemistry* 65, 1524–1528.
- Obata, H., Karatani, H., Matsui, M., Nakayama, E., 1997. Fundamental studies for chemical speciation of iron in seawater with an improved analytical method. *Marine Chemistry* 56, 97–106.
- Obata, H., Nozaki, Y., Alibo, D.S., Yamamoto, Y., 2004. Dissolved Al, In and Ce in the eastern Indian Ocean and the Southeast Asian Seas in comparison with the radionuclides  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ . *Geochimica et Cosmochimica Acta* 68 (5), 1035–1048.
- Ober, S., Groenewegen, R.L., Boekel, H.J., Keijzer, E.J.H., Derksen, J.D.J., Laan, M., 2002. A new way of oceanographic watersampling. Abstract of presentation at Inmartech, 8 October 2002, Yokusuku, Japan. <http://www.jamstec.go.jp/jamstec-e/whatsnew/inmartech2002/program.pdf>.
- Parekh, P., Follows, M.J., Boyle, E.A., 2005. Decoupling of iron and phosphate in the global ocean. *Global Biogeochemical Cycles* 19, GB2020. doi:10.1029/2004GB002280.
- Patterson, C.C., 1956. Age of meteorites and the Earth. *Geochimica et Cosmochimica Acta* 10, 230–237.
- Patterson, C.C., Settle, D.M., 1976. The reduction of orders of magnitude errors in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collection and analysis. *Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis*. U.S. NBS Special Publication.
- Saito, M.A., Schneider, D.L., 2006. Examination of precipitation chemistry and improvements in precision using the  $\text{Mg}(\text{OH})_2$  preconcentration inductively coupled plasma mass spectrometry (ICP-MS) method for high-throughput analysis of open-ocean Fe and Mn in seawater. *Analytica Chimica Acta* 565, 222–233.
- Sarthou, G., Laan, P., Ussher, S., Kramer, J., Timmermans, K.R., Blain, S., 2003. Influence of high atmospheric inputs on the iron distribution in the water column of the North Atlantic Ocean. EGU/AGU; Joint Assembly Nice, France, 07–11 April 2003.
- Sarthou, G., Baker, A.R., Kramer, J., Laan, P., Laës, A., Ussher, S., Achterberg, E.A., De Baar, H.J.W., Timmermans, K.R., Blain, S., 2007. Influence of atmospheric inputs on the iron distribution in the subtropical North-East Atlantic Ocean. *Marine Chemistry* 104, 186–202.
- Schaule, B.K., Patterson, C.C., 1981. *Earth and Planetary Science Letters* 54, 97.
- Slater, F.R., Boyle, E., Edmond, J.M., 1976. On the marine geochemistry of nickel. *Earth and Planetary Science Letters* 31, 119–128.
- Skrabal, S.A., 2006. Dissolved titanium distributions in the Mid-Atlantic Bight. *Marine Chemistry* 102, 218–229.
- Spencer, D.W., Brewer, P.G., 1971. Vertical advection, diffusion and redox potentials as controls on the distribution of manganese and other trace metals dissolved in waters of the Black Sea. *Journal of Geophysical Research* 76, 5877–5892.
- Timmermans, K.R., et al., 2006. New European facility for ultraclean sampling of trace elements and isotopes in the oceans in the Geotraces program. Abstracts at: February 2006 AGU/ASLO Ocean Sciences, *Eos Trans. AGU*, 87(36); European Geosciences Union, Vienna, April 2006, EGU 06-A-03163; AGU Fall Meeting, San Francisco, December 2006.
- Ussher, S.J., Worsfold, P.J., Achterberg, E.P., Laës, A., Blain, S., Laan, P., de Baar, H.J.W., 2007. Distribution and redox speciation of dissolved iron on the European Continental Margin. *Limnology and Oceanography* 52 (6).
- Warnken, K.W., Tang, D., Gill, G.A., Santschi, P.H., 2000. Performance optimization of a commercially available iminodiacetate resin for the determination of Mn, Ni, Cu, Cd and Pb by on-line preconcentration inductively coupled plasma-mass spectrometry. *Analytica Chimica Acta* 423, 265–276.
- Wu, J., Boyle, E., 2002. Determination of iron in seawater by high-resolution isotope dilution inductively coupled mass spectrometry after  $\text{Mg}(\text{OH})_2$  coprecipitation. *Analytica Chimica Acta* 367, 183–191.
- Wu, J.F., Boyle, E., 2002. Iron in the Sargasso Sea: implications for the processes controlling dissolved Fe distribution in the ocean. *Global Biogeochemical Cycles* 16 (4), 464–471.