



*Dedicated to the memory of Professor Margareta Avram
on the remembrance of her 100th anniversary*

CORRELATION OF ISOCONCENTRATION PROFILES RESOLUTION OF WATER PARAMETERS WITH ON-SITE SAMPLING METHODOLOGY

Mariana Carmela HORJA,^a Daniela ISTRATI,^{a*} Ioan CALINESCU,^a Dan Eduard MIHAIESCU,^a
Anca Liana MARTON,^a Alexandru IONESCU^b and Gheorghe UNGUREANU^c

^a Politehnica University Bucharest, Splaiul Independentei 313, Bucharest – 060042, Roumania

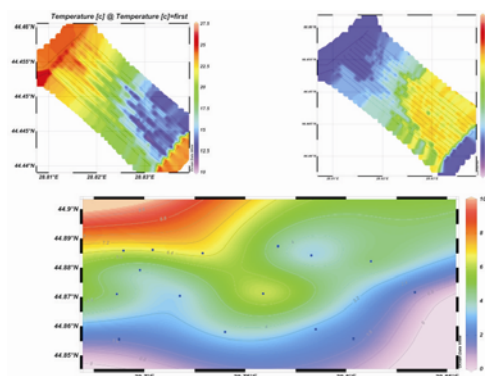
^b SC Marine Research SRL, Copilului 6-12, Bucharest – 012244, Roumania

^c University of Bucharest, M. Kogălniceanu 36-46, Buharest – 010018, Roumania

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Water parameters screening is a constant request for conservation state evaluation in protected areas. Classic methods are using sampling stages and laboratory transfer for instrumental analysis process. Related to analytical data request, new on-site methods were developed, from the basic water parameter measurements (like those used in **CTD** (*Conductivity-Temperature-Depth Sampler*) or multiparameter extended sensor based system) to the detection of organic pollutants trace levels, like those used in the high performance on-site UW-MS (*Underwater Mass Spectrometer*) systems.

The aim of our work was to evaluate sampling point variability and to compare the data point resolution differences by using classical and new on-site screening methods. Isoconcentration profiles of water parameters linked to a conservation state study for protected areas at Black Sea border were used for this purpose. The sampling expeditions and on-site screening stages were performed in two seasons: 2011 and 2012. Both methods were used: laboratory analysis for advanced water parameters and on-site screening for basic parameters, using CTD (multiparameter) and AUV systems.



INTRODUCTION

Oceans are one of most important assets of our planet, being the starting point for life development. Understanding the ocean natural environment was always one of the most challenging dreams. Ocean water dynamics is by far one of the most important processes at global scale due to the endorsement of almost all our economical and social activities, providing from oxygen, to the complex food chain and planetary temperature regulation. The fast, global climate changes and the accelerated natural

environment degradation confronted us with the results of our behavior as resident of the top position in the trophic chain, due to the lack of awareness, respect and love for our natural environment. The wild exploitation of almost all possible natural resources caused the disruption of global equilibrium sustaining life on our planet. One of the consequences of such behavior may derive from a possible extrapolation of the well-known *Le Châtelier* action-reaction principle. As a feedback to the pollution, in the worst Forsythe scenario, a next planetary equilibrium may no more

* Corresponding author: d_istrati@yahoo.com

include *Homo sapiens* (with the ironic translation: “wise man”). Such hypothesis should not turn into reality if we could honestly place ourselves not as “disturbance factor”, but as a catalyst for ecological equilibrium restoration.

In such context of global climate change, and increasing pollution sources, water monitoring is a useful tool in the efforts for protected area conservation, supported by the new on site analysis methods recently developed. An important research and technological effort was focused on developing commercial on-site screening tools like: CTD (conductivity-temperature-depth sampler) and multiparameter systems, AUV (Autonomous Underwater Vehicle), advanced multisensor AUV platforms, and other high performance analytical methods using UW-MS (Under Water Mass Spectrometer), last generation spectrophotometers, particle size analyzers, gas sensors and others. The huge data volume, accessible by these on-site analysis methods, appealed to specific computer – based numeric analysis and integration methods. An example is the design of Geographical Information Systems (GIS), a simple tool used to depict the distribution of the relevant parameters, having applications in various fields. GIS have been used for developing the Oceanographic Information System (OIS) for marine environmental data. The aim of this system is to provide a set of tools for oceanographic and bathymetry data assessment and products like graphs query system for the users. The most important interfaces are the GIS based Map-query and Contour visualization. The interfaces are user friendly and oriented towards bridging the gap between user's knowledge and the technical knowledge required to operate the software system. Last, but not least, the OIS also provides users with several analytical tools, like query-based reports and graphs. An important step

in data analysis is related to variability assessments, method validation and correlation of the results with the conservation state of the ecosystems.

RESULTS AND DISCUSSION

The data analysis step, quite challenging due to the huge data amount, was structured in 7 sections:

- A. Sampling point variability study;
- B. CTD and AUV basic data analysis;
- C. Metals, pesticides and PAH analysis;
- D. Data integration;
- E. Elaboration of isoconcentration profiles;
- F. Defining conservation levels*;
- G. Elaboration of conservation state evaluation methodology*.

(* – items not included in the present work)

A. Sampling point variability study

The sampling point variability study was performed using the described methodology and provides significant data used to further on-site sampling. According to these results, in the area of 120x120m the parameter variability (evaluated as standard deviation of the values obtained in the depth level) a good statistical homogeneity was detected, with a percent deviation lower than 5% related to the mean value. These results prove that the sampling procedure can be considered relevant for the monitored water parameters, also in the case of a possible vessel drift during the sampling process.

Fig. 1 and Fig. 2 exemplify the results for the SPLINE function raw data interpolation for a CTD readout (sampling point 3), the depth level plane 3D image and the combined 3D image for all 5 planes related to the 1 – 5m depth levels resulted values.

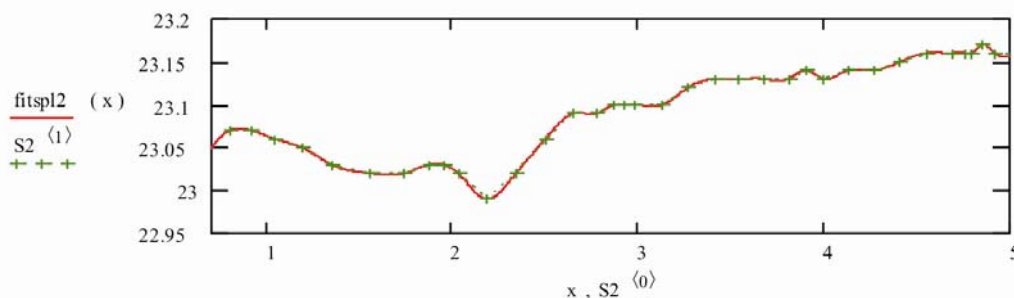


Fig. 1 – SPLINE raw data interpolation for a CTD readout (conductivity – sampling point 3), cond. [mS/cm] – dept[m] of the 5 planes used in the sampling point study.

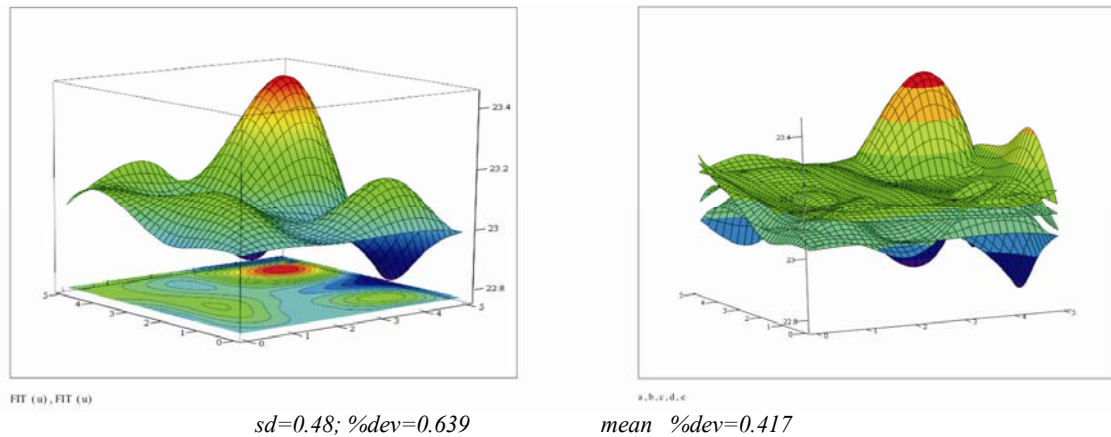


Fig. 2 – 3D image of the depth level plane (using SPLINE data row interpolation of the 4x4 sampling points) and the combined 3D image.

B. CTD and AUV basic data analysis

Both, AUV and CTD raw data were processed using the described methodology and isoconcentration profiles were obtained for all monitored water parameters. Fig. 3 and Fig. 4 exemplify the ODV profiles from two sampling stages (one AUV mission and one day CTD sampling stage).

As expected, AUV data are significantly detail – focused related to the monitored parameter, because of the high data acquisition rate, but

obtaining depth profile data is quite difficult related to several missions programmed at different depths. CTD data are significantly less detailed due to isoprofile containing less data points but provide much more information for the depth profile. As a conclusion, CTD data is relevant for larger area coverage, and AUV data is very useful for a localized, detail-focused study (limited by the device autonomy to 7-8 hours and by the vessel battery recharge time).

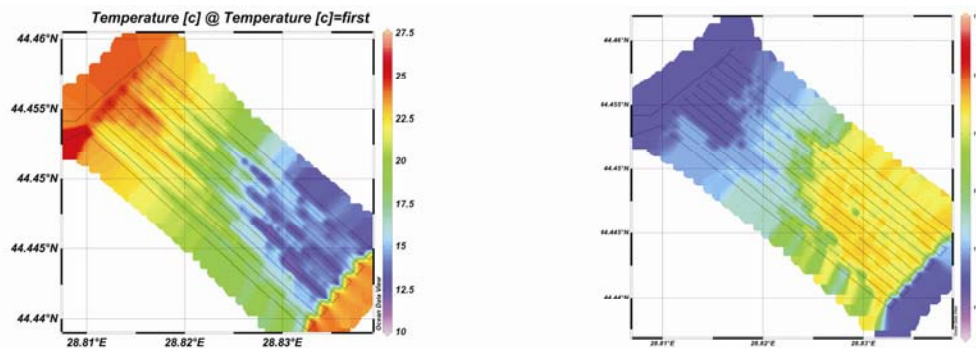


Fig. 3 – Isoconcentration profile (salinity [PSU] correlated with temperature [°C] – left image) for one AUV mission at Chituc perimeter – 22750 data points, dept 3m.

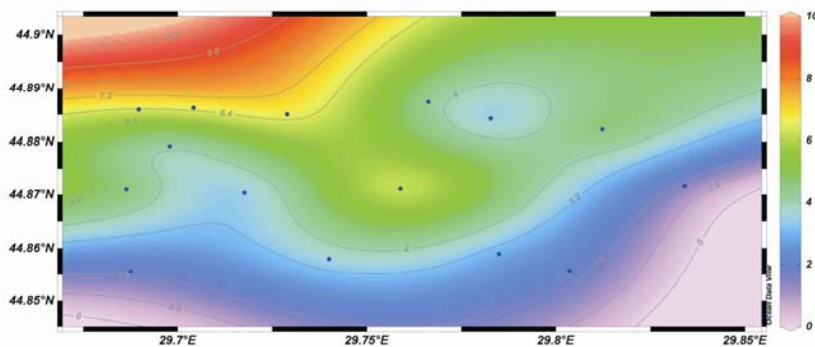


Fig. 4 – Isoconcentration profile for chlorophyll A [mg/l], by CTD determination (one meter and 10 m depth, from ODV, near the Sfântu Gheorghe village at Danube mouth – 15 sampling points).

C. Metals, pesticides and PAH analysis

Similar profiles were obtained for all monitored water parameters and all *Natura 2000* parameters

included in the study. Figs. 5–7 exemplify metals, pesticides and PAH isoconcentration profiles resulted by ODV data processing.

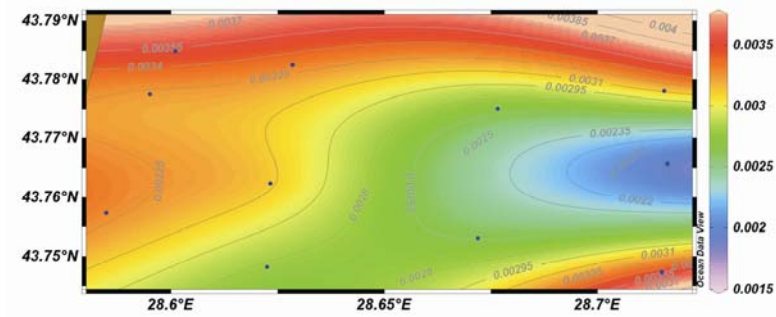


Fig. 5 – Isoconcentration profile for Pb [ppm], *Vama Veche* protected area (ICP-OES method), 4 m depth.

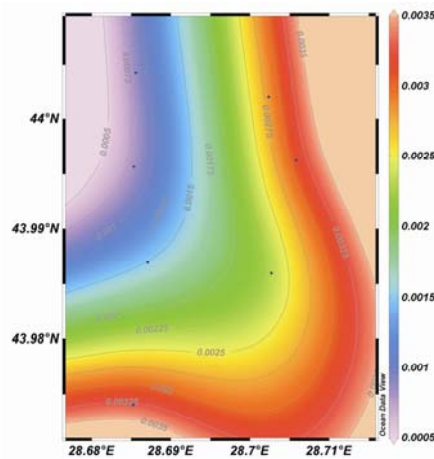


Fig. 6 – Isoconcentration profile for alachlor [ppm], *Tuzla* protected area (GC-MS method), 1m depth.

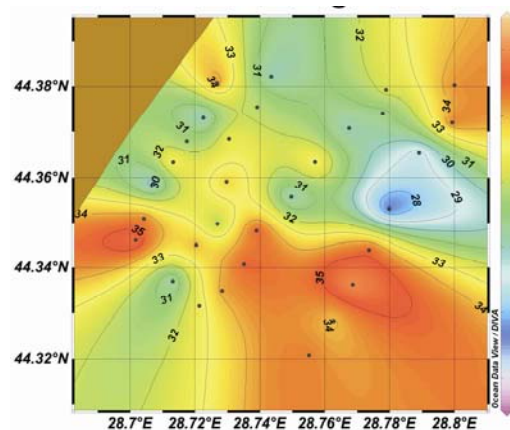


Fig. 7 – Isoconcentration profile for anthracene [ppb], *Vadu* protected area (GC-MS method), 1m depth.

D. Data integration, elaboration of isoconcentration profiles

ODV georeferenced isoconcentration images were included as a transparency-optimized plane in the

whole Global Mapper image of the specific monitored perimeter, obtaining the final image with relevant information like parameters variability (exemplified for salinity in Fig. 8) and pollutants spreading (exemplified for Dacthal in Fig. 9) in the defined area.

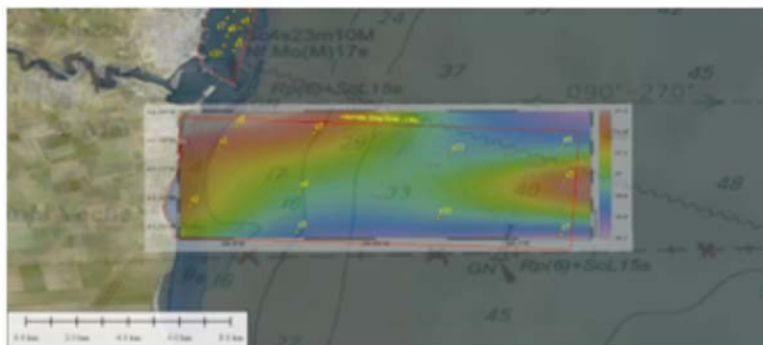


Fig. 8 – Isoconcentration profile for salinity related to the 2-Mai-Vama Veche Natura 2000 protected area (PSU units).

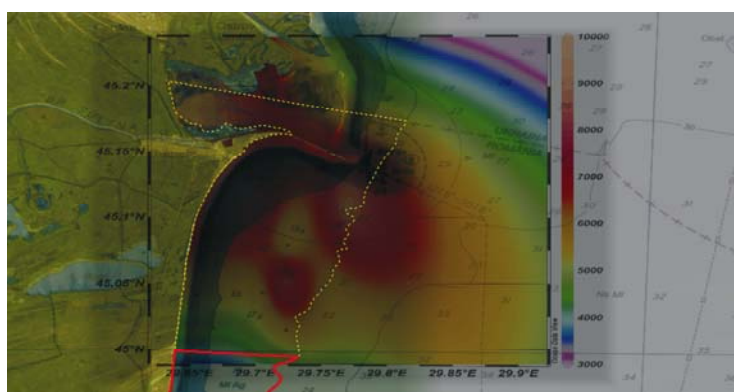


Fig. 9 – Isoconcentration profile for Dacthal at Sulina Natura 2000 protected area (ppt units).

In order to obtain the GIS integrated isoconcentration profile, several experimental steps were performed for both – lab-based analysis and on-site analysis.

For lab-based analysis (measurements of anthracene – Fig. 7,alachlor – Fig. 6, dacthal – Fig. 9, lead – Fig. 5), the experimental steps were:

- sampling perimeter assignment and sampling expedition planning by GPS route planning and sampling point assignment – Global Mapper software was used for this purpose, the sampling stations were assigned by a grid with equally distributed sampling points, usually 45–70 sampling points per workday were established;
- sample collection by the sampling expedition;
- sample transfer to the laboratories;
- sample extraction, purification and analysis following the PAH method for anthracene, OCL method foralachlor and ICP method for lead:

- by PAH method: 1000 mL sample were extracted by 3x50 mL hexane, using a separation funnel, dried with 30 g anhydrous Na_2SO_4 , purified by a flash florisil column and concentrated at 1 mL by rotavap for the GC-MS injection (GC: 30m DB5-MS column, 0.25 mm id, 0.25 m film thickness, temp. program 60-270°C-5 grd/min, 280°C

injector temp., SSL 1.0 min splitless time / 60 mL/min purge flow, 3 uL injection, 230°C transfer line temp., MS: SIM method – for anthracene 178 amu quant peak and 179/76 as qualifier); the quantification method involved blank and 6 calibration samples from reference mix in the 10 – 80 ppb range, at least 0.995 correlation coefficient as qualifying value for the linear regressions of all target compounds was used;

- by OCL method: 1000 mL sample were extracted by 3x30 mL dichlormethane, using a separation funnel, dried with 30 g anhydrous Na_2SO_4 , purified by a flash florisil column and concentrated at 1 mL by rotavap for the GC-MS injection (GC: 30 m DB5-MS column, 0.25 mm id, 0.25 m film thickness, temp. program 40-110°C-20 grd/min - 280°C-4grd/min, 280°C injector temp., SSL 1.0 min splitless time / 60 mL/min purge flow, 3 uL injection, 230°C transfer line temp., MS: SIM method – foralachlor 178 amu quant peak and 179/76 as qualifier, for dacthal 178 amu quant peak and 179/76 as qualifier); the quantification method involved blank and 6 calibration samples from reference mix in the 1–50 ppb range, at least 0.994 correlation coefficient as qualifying

value for the linear regressions of all target compounds was used;

- by ICP-OES method: 50 mL sample were acidified at 1.0% with HNO₃; the quantification method involved blank and 6 calibration samples in NaCl matrix, from reference mix in the 1 – 100 ppb range for trace level metals, at least 0.994 correlation coefficient as qualifying value for the linear regressions of all target compounds was used.
- data analysis and correlation with GPS data, file formatting for ODV software;
- isoconcentration image setup by ODV software;
- integration of the isoconcentration image in the whole GIS image, together with satellite images, sampling cruise plan and bathymetric images;
- final analysis of the GIS integrated isoconcentration profile.

For on-site analysis (measurements of salinity – Fig. 3, 8, chlorophyll – Fig. 4 and sampling point validation study), the experimental steps were:

- I. CTD (Emma Technology) and AUV (Iver 2) platform startup, and mission setup by GIS correlation for AUV;
- II. all CTD and AUV measurements were performed by using the factory calibration data of all sensors (for CTD measurements – temperature, water column pressure, salinity, chlorophyll, magnetometry, photosynthetic active radiation – PAR; for AUV measurements – temperature, water column pressure, salinity), because all sensor calibrations were performed periodically, by the supplier of the equipment;
- III. data transfer and analysis, respectively GIS integration steps, were performed by using the same data processing stages, already described for the lab-based analysis.

EXPERIMENTAL

A. Sampling point variability study

One of the first approaches of this study was related to the understanding of sampling point variability, in order to obtain representative samples for advanced laboratory analysis like ICP-OES and GC-MS. For this target we define a sampling point variability study a parallelepiped, as presented in Fig. 10 and Fig. 11, with 120 x 120m area and 5m depth with 4 sampling points per line in the isosurface plane. The vessel course line was defined after establishing the sampling location by using Global Mapper software for the scientific expedition route planning (Fig. 10).

Coordinates of the sampling stations were defined as: 44° 53' 43.5225" N, 29° 38' 31.4819" E for S1, 44° 53' 46.3106" N, 29° 38' 32.6851" E for S4, 44° 53' 45.4582" N, 29° 38' 36.6209" E for S13 and 44° 53' 42.6701" N, 29° 38' 35.4176"

E for S16, in the *Sfântu Gheorghe Natura 2000* protected area (near to the *Sfântu Gheorghe* village at Danube mouth).

The sampling stage involves CTD measurement for every defined sampling point (red points, Fig. 11) 1 L water samples for every point and also deep profile points by pump sampling (for ICP-OES and other determinations).

The vessel used for the sampling point validation study was a Beneteau Antares (Explorer).

Pump sampling was performed by an immersed 12V pump with 10 liter/min flow (we used a 12 V battery and solar panel autonomous system, in order to preserve the boat battery for lasting). A 2 min pumping flush time was used to insure accurate sampling. Samples were stored in polypropylene single use clamp-bags. The CTD measurements were done using a 0.1 decibar sampling rate.

For the sampling point variability study, a minimal set of analysis were performed: the CTD sensor, based analysis (temperature, conductivity, pH, redox potential, salinity, chlorophyll, oxygen concentration) together with the ICP-OES laboratory analysis. For the data analysis step, we built a small 3D visualization tool using MATHCAD, in order to draw a variability image for the 1, 2, 3, 4 and 5 m planes. For the CTD data, a SPLINE profile was drawn for every data row, in order to find the exact values for the defined planes, to build the whole variability image. Also the plane standard deviation and the global parallelepiped standard deviation were obtained for every defined water parameter. The variability 3D image and the conclusions of the sampling point variability study were presented at the Results and Discussions section.

B. Sampling stages

The sampling expeditions were divided in several sections in the 2011 – 2013 period, using 5 research vessels and a significant team effort to cover the huge *Natura 2000* protected sea area (shoreline up to the 20m depth).

C. CTD and AUV data acquisition

The sampling expeditions were divided in two: sea expeditions for CTD and water sampling and land expeditions for the AUV data acquisition. The characteristics of the CTD system are: EMMA Technologies Multiparameter system with pressure, temperature, conductivity, redox potential, oxygen, chlorophyll, PAR sensors. The characteristics of the AUV systems are: Ocean Server Technology IVER 2 with side scan sonar, conductivity and temperature sensors.

All data were exported in .csv (comma separated values) format from the dedicated AUV and CTD software and used further for the data processing step. At this step, MATHCAD and Libre Office Calc software were applied in order to export data-rows in an ODV compatible format (Schlitzer, R., Ocean Data View, <http://odv.awi.de>, 2014). At the final stage, the ODV georeferenced isoconcentration image was included as a transparency-optimized plane in the whole Global Mapper image (the base image was obtained using several planes with specific images: bathymetric maps, satellite images from NASA and Google Map) of the selected area (a similar procedure was used for the obtained isoconcentration profiles).

D. Laboratory analysis

The laboratory analysis (ICP-OES and GC-MS) were performed using a THERMO SCIENTIFIC iCAP 6000 Duo ICP-OES using TEVA data analysis software, 1100W plasma power at 27.12 MHz, and a AGILENT 5975 MS / 6890 GC with autosampler, using Chemstation data analysis software. The metals, pesticides and PAH analysis were performed using EPA-based methods.



Fig. 10 –Scientific expedition route planning for sampling point validation.

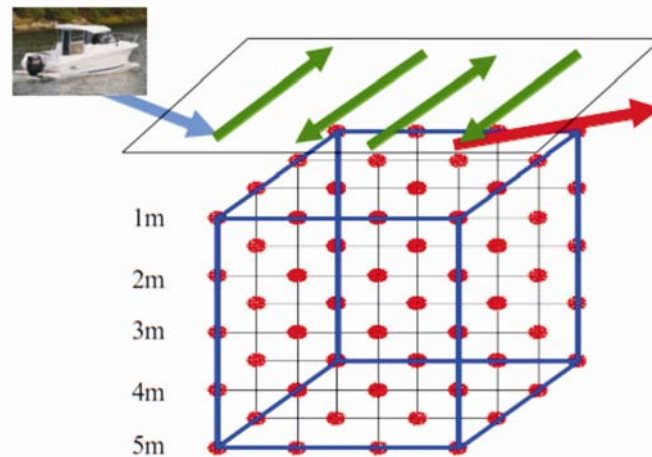


Fig. 11 – Sampling point variability study parallelepiped (sampling points not at scale).

CONCLUSIONS

The main conclusions of our study are:

- using a variability study before sampling is an important step for sampling point profile definition; AUV and CTD sampling can provide very useful complementary information related to the conservation state of habitats and species in protected areas;
- obtaining isoconcentration profiles for as much as possible water parameters is certainly one of the best method to obtain a useful overview of physico-chemical parameters of water;
- on site screening methods provide significantly better resolution for isoconcentration maps with a decreased cost per sample ratio.

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