ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

ISMAR Istituto di Scienze Marine
Consiglio Nazionale delle Ricerche

Characterization of the coastal area facing Cogoleto (Ligurian Sea): Areal and historical distribution of chromium

R.M. Bertolotto, F. Gaino, L. Bellucci, S. Giuliani, S. Romano, M. Frignani

ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

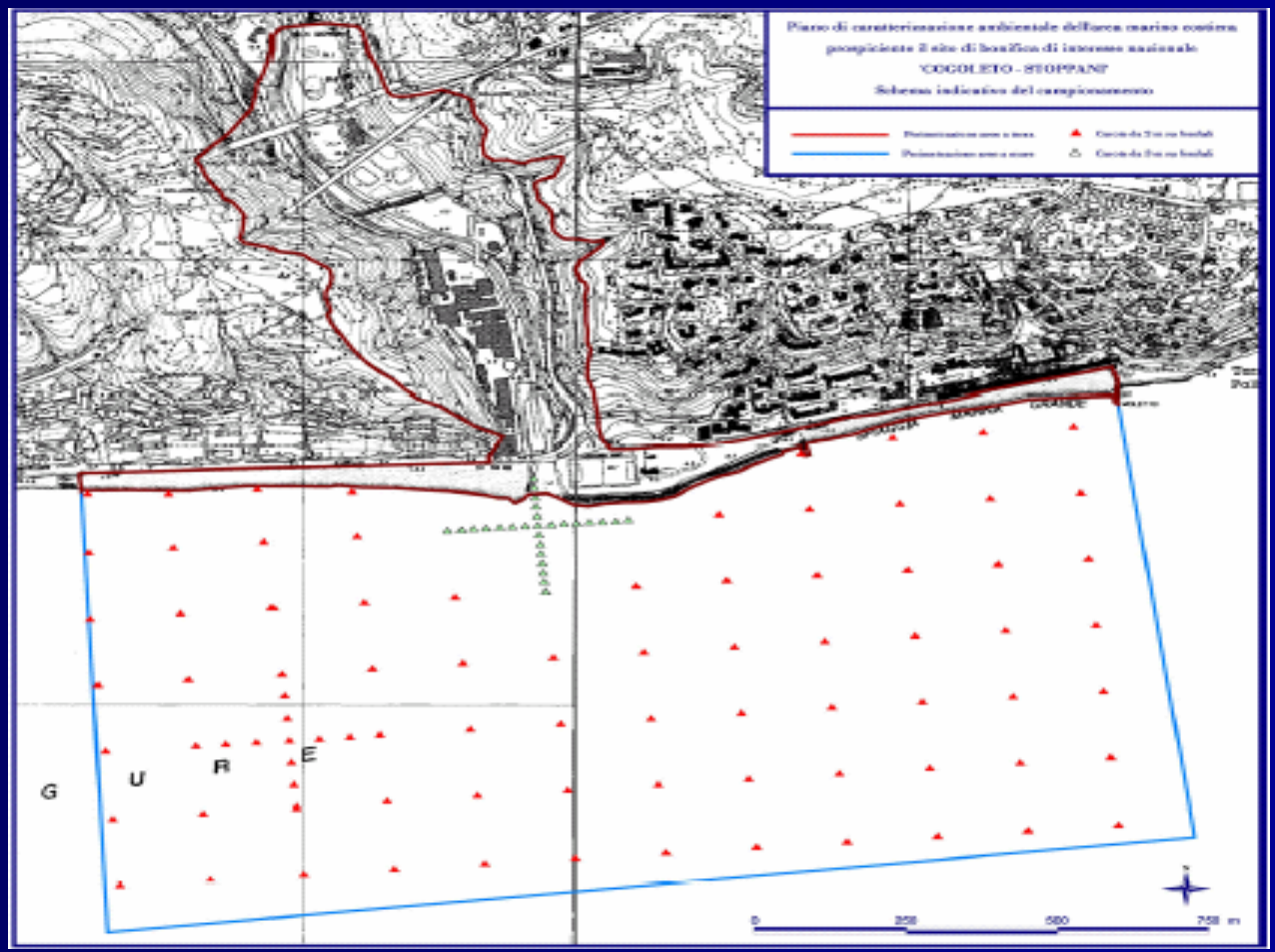
Presentation layout

- Site description
- Characterization study (Arpal, 2004)
- Complementary study (Arpal- ISMAR-CNR, 2005)
- Conclusions

ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

Remediation site of Cogoleto-Stoppani (Genova- Northern Italy)



ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

About the area

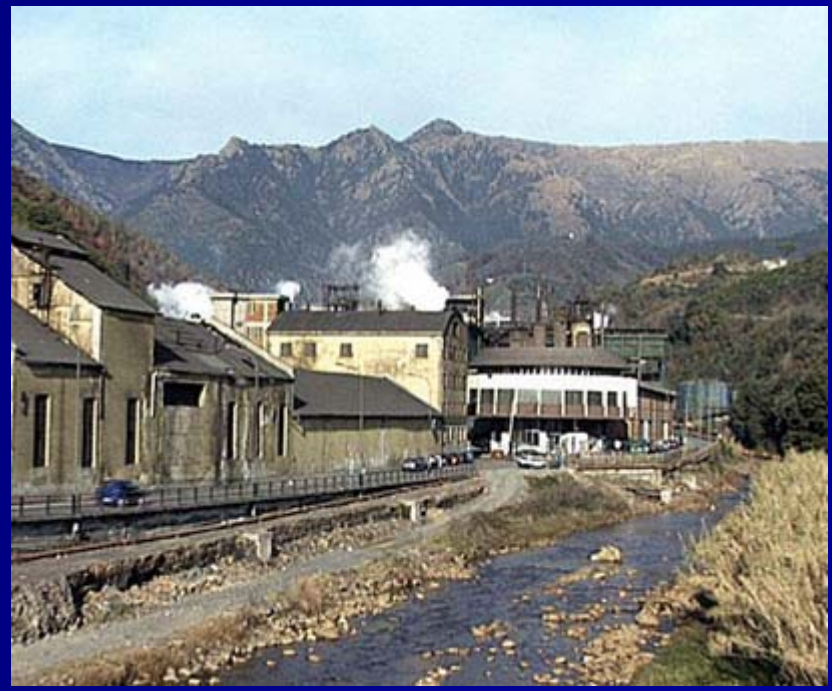
- Area surrounding Lerone river mouth, both on the ground and in the sea
- Lithological description: peridotites, serpentines with basalt inclusions
- Chromium- rich rocks
- Marine area: *Posidonia Oceanica* meadows on soft bottom
- Hardened bottom near the river mouth, probably because of past industrial discharges into the sea

ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

Area subjected to heavy pressures

Haven wreck- April 1991

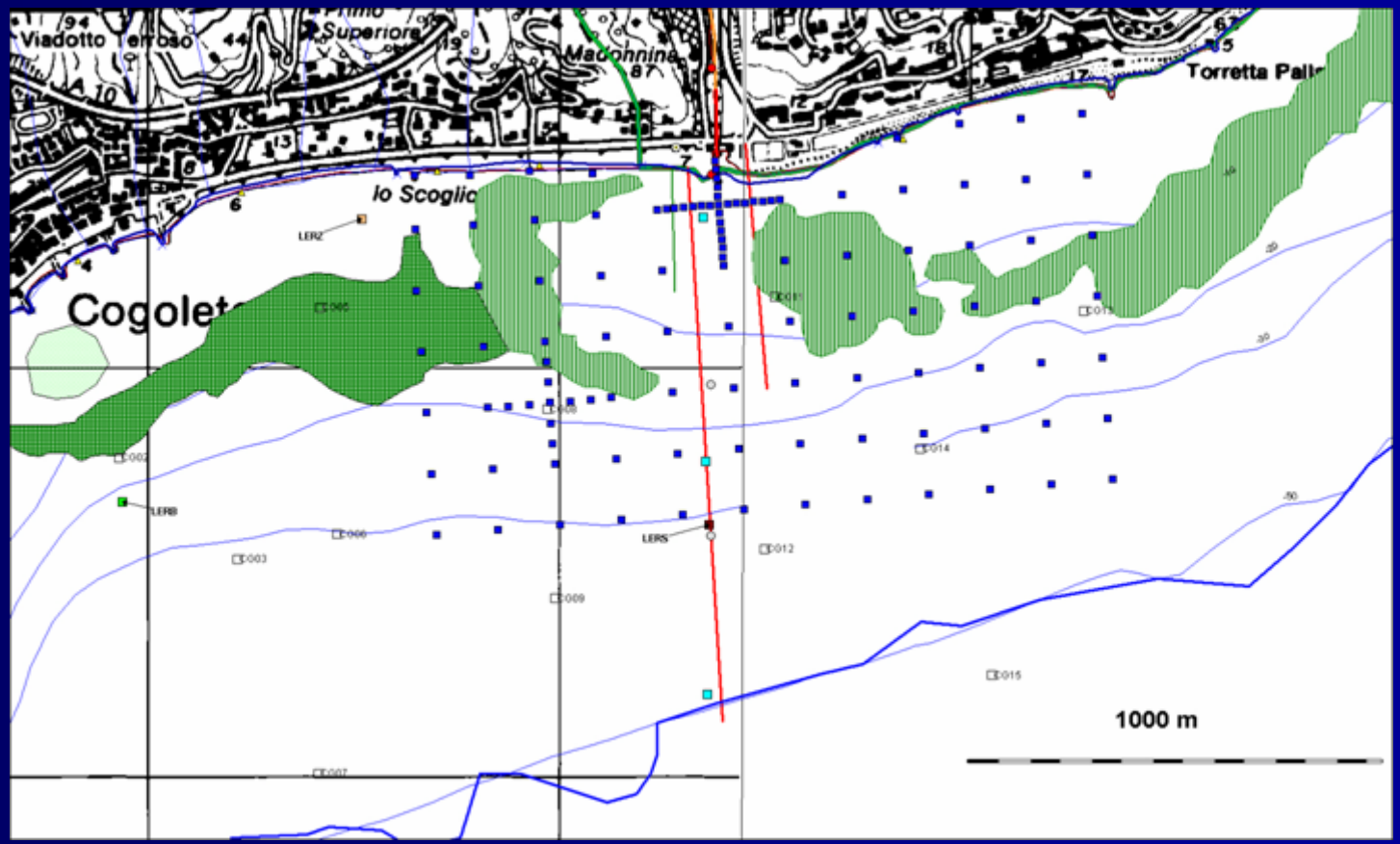


Stoppani- Production of Chromium derivatives since 1900

ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

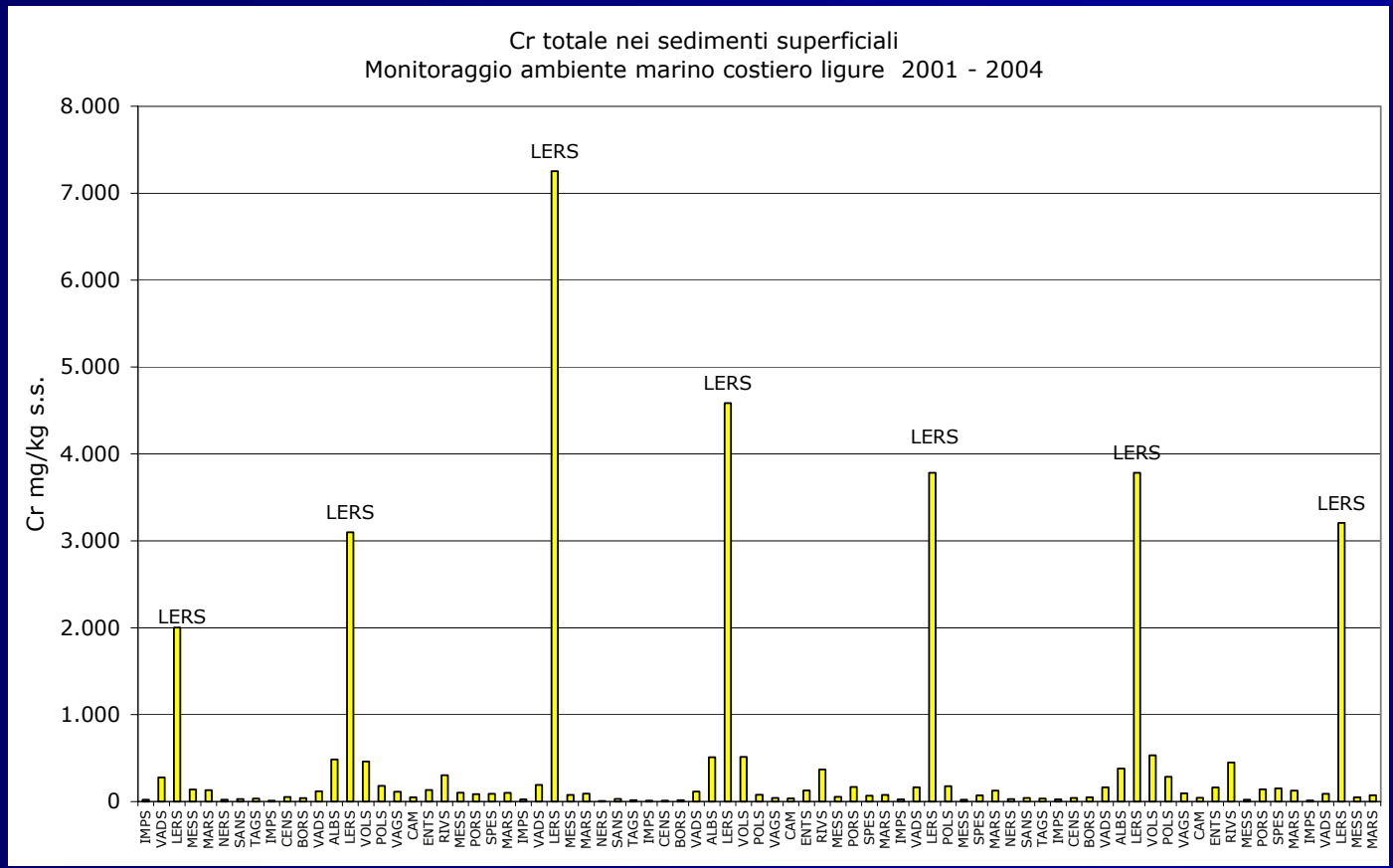
Posidonia oceanica meadows



ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

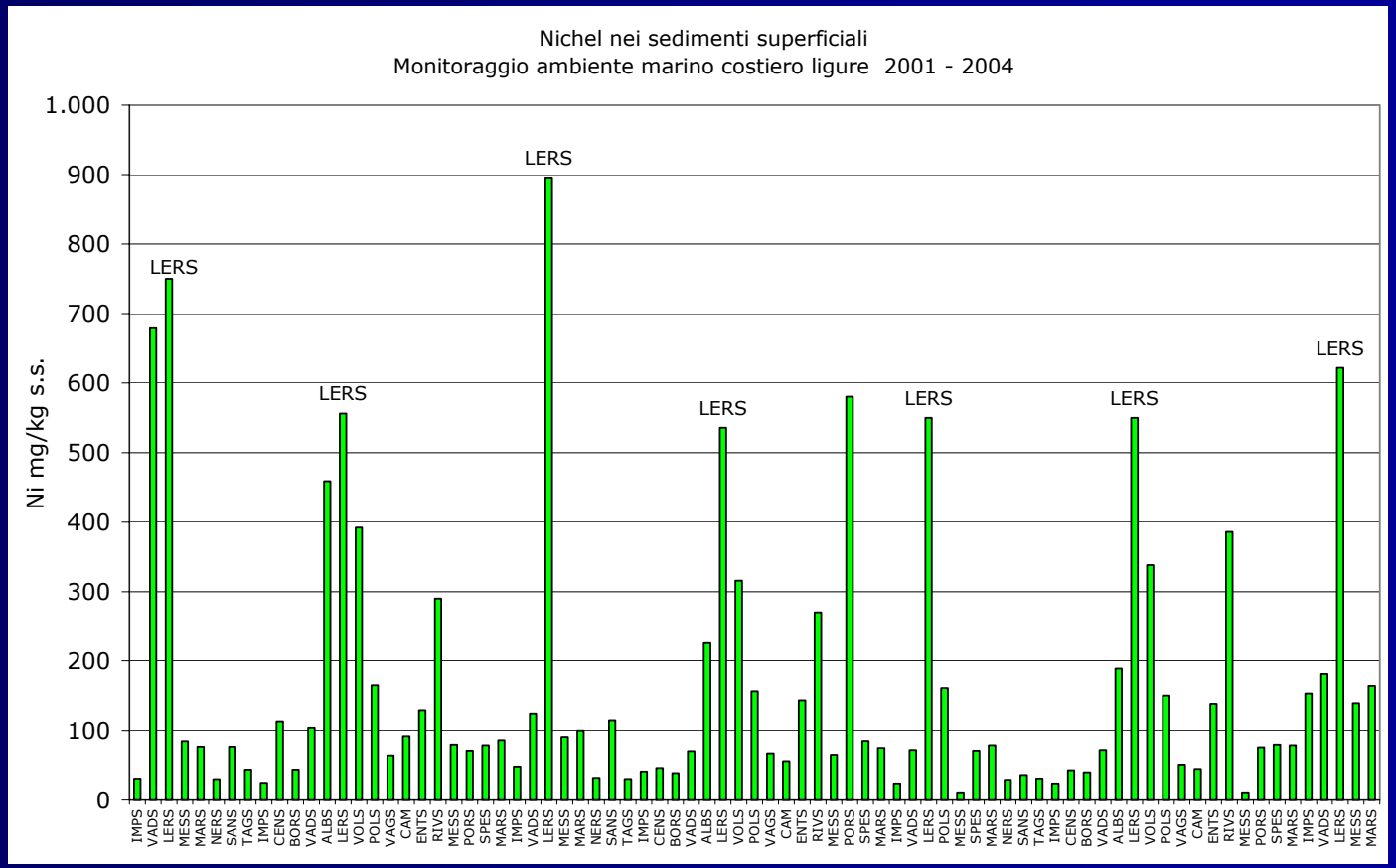
Coastal monitoring 2001-2004 Chromium in sediments along Ligurian coast



ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

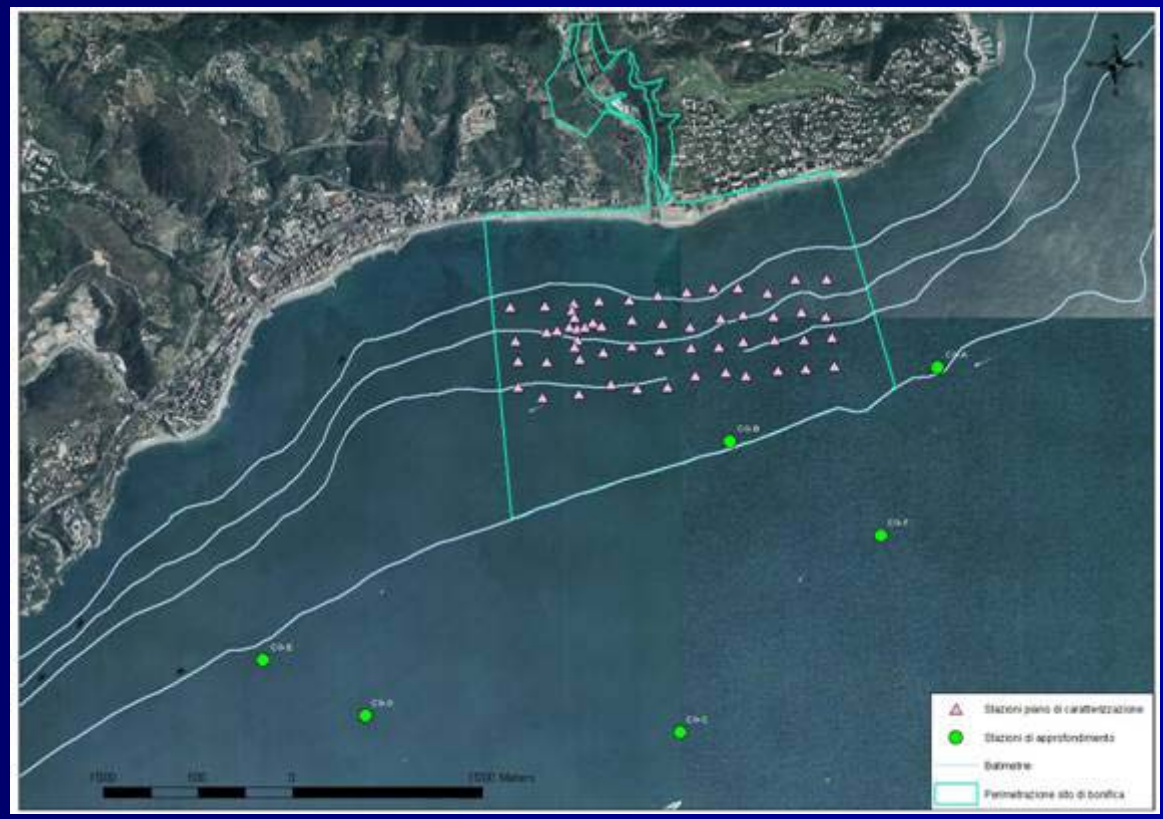
Coastal monitoring 2001-2004 Nickel in sediments along Ligurian coast



ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

Study area and sampling locations



Pink : site characterization sampling points
Green: complementary study sampling points

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

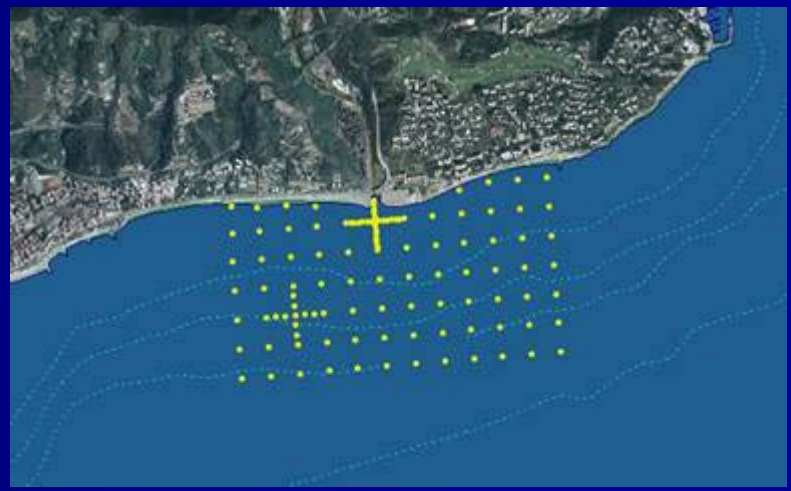
Site characterization / 1

- use of vibrocorer
- 57 cores 200-300 cm
- 5 or 6 sections from each core
- 0-10 cm, 10-30 cm, 30-50 cm, 100-120 cm, 180-200 cm, 280-300 cm (for longer cores)
- pH, redox, stratigraphic description and subsampling *in situ*
- 222 samples analyzed

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

Site characterization / 2

- Physical parameters *:* granulometry, water content, specific weight
- Chemical analyses: Metals (Al, As, Cd, Co, Cr tot, Cr VI, Cu, Fe, Hg, Mn, Ni, Pb, V, Zn, PAHs, PCBs, HC, Cyanides, N, P, TOC, dioxins, furanes, TBT, asbestos)
- Microbiological analyses: *Strepto. faecalis, Salmonella,* Sulfite-reducing Clostridium spores



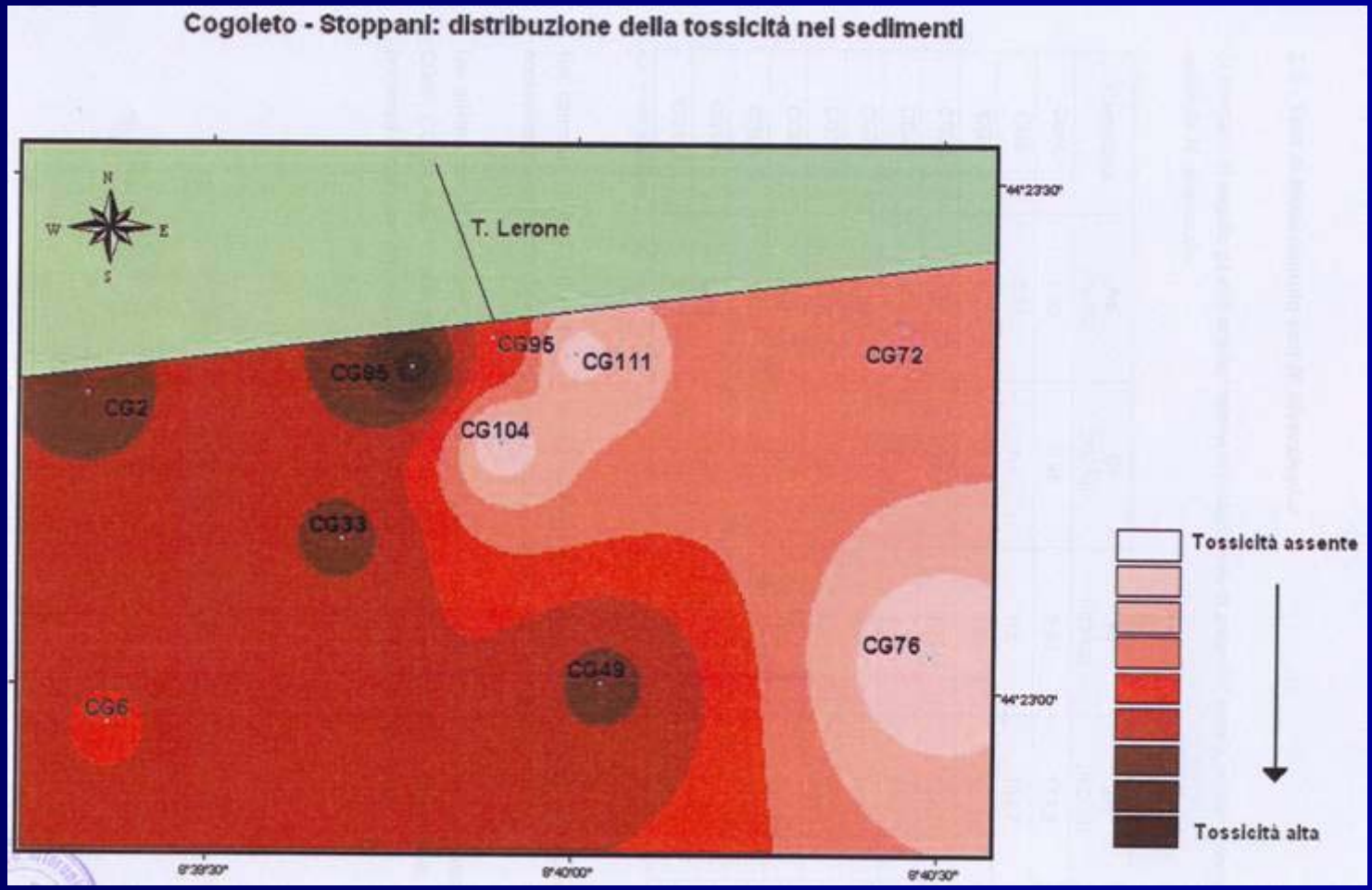
- Ecotoxicological tests with *Vibrio Fischerii, Corophium Orientale, Paracentrotus Lividus*
- Bio-accumulation test with *Hediste Diversicolor*

ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

Site characterization / 3

Sediment toxicity



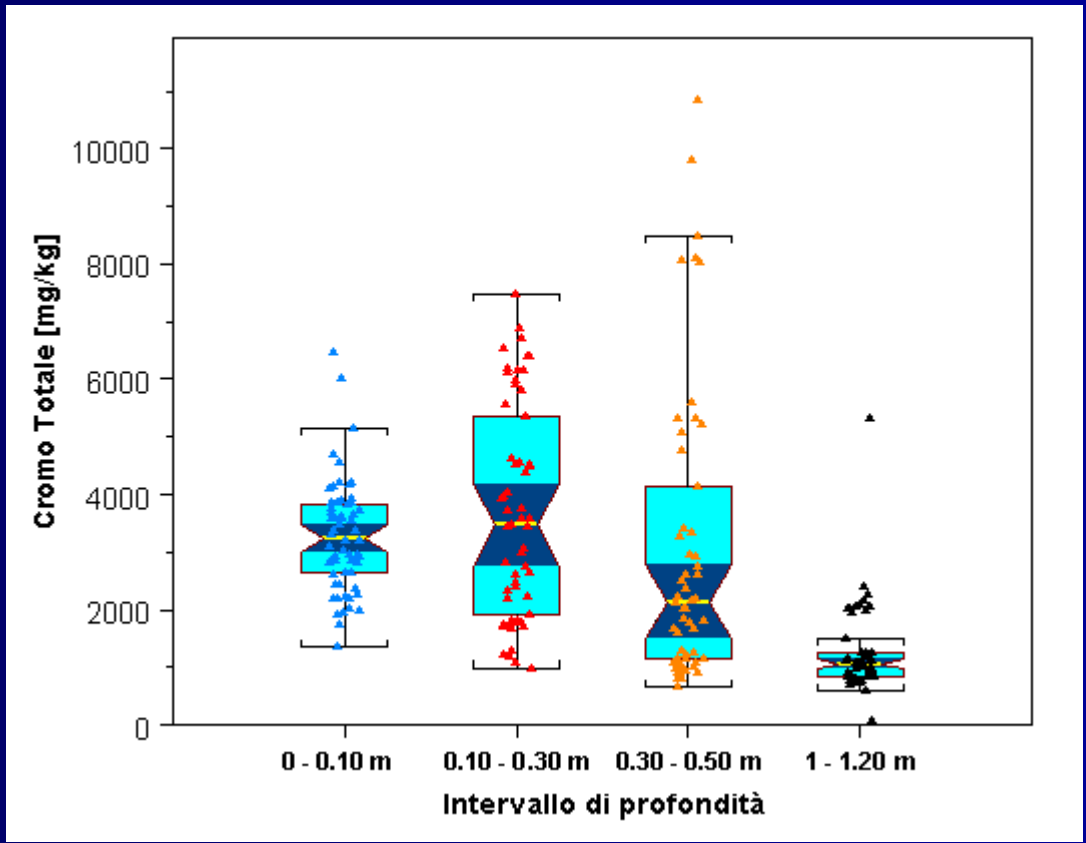
ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

Site characterization / 4 Findings

- The area is deeply contaminated by heavy metals (total chromium, nickel)
- Cr concentrations are maximum in surficial or subsurficial layers, mainly West of Lerone river mouth
- Toxicity decreases from Lerone river eastwards (main current is westwards)
- Part of the area is covered by a “concrete” layer, still to be characterized in depth and width, but with the same chemical composition as the surrounding “soft” sediments
- A “background value” for Chromium in this area has been calculated with a statistical method

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

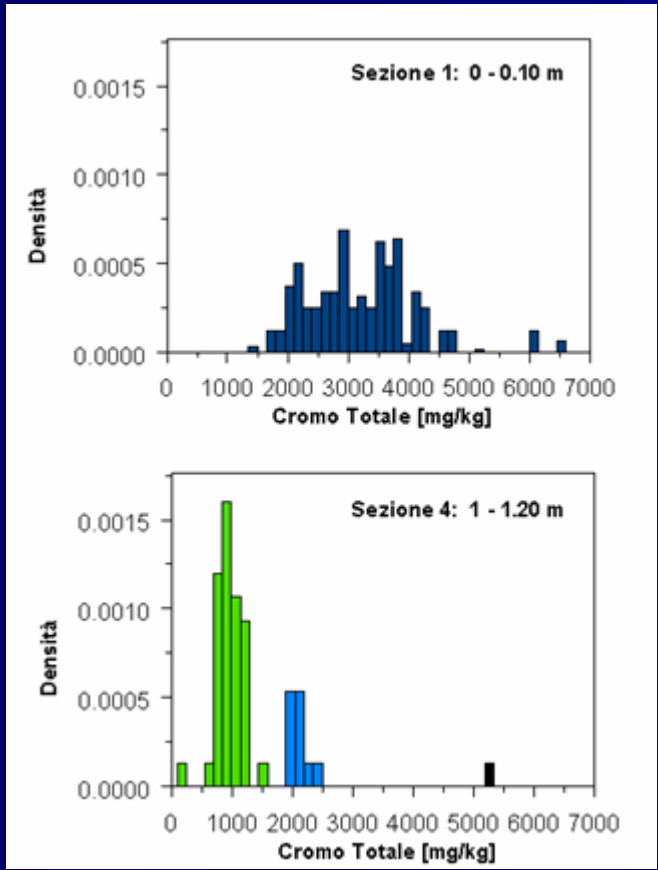
Site characterization / 5
Looking for a natural Cr background value



Box-plot

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

Site characterization / 6
Looking for a natural Cr background value



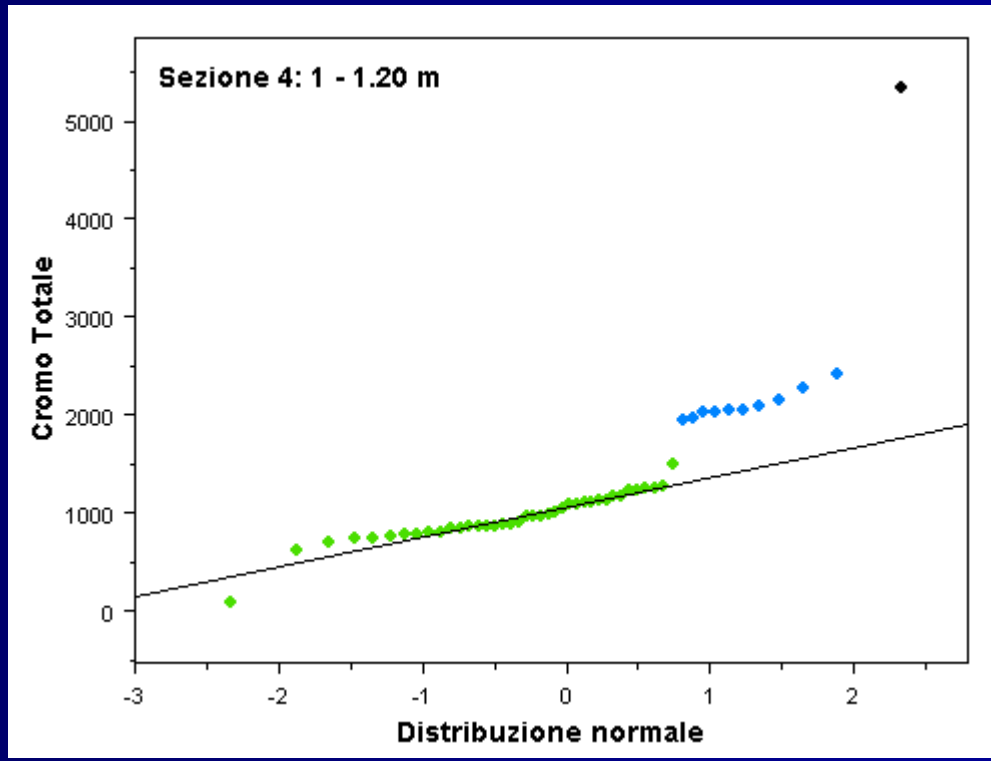
In the surficial layers chromium concentrations tend to be continuously distributed

In deep layers the histogram shows a bi-modal nature with two groups of concentrations

500-1500 mg/kg
1500-2500 mg-kg

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

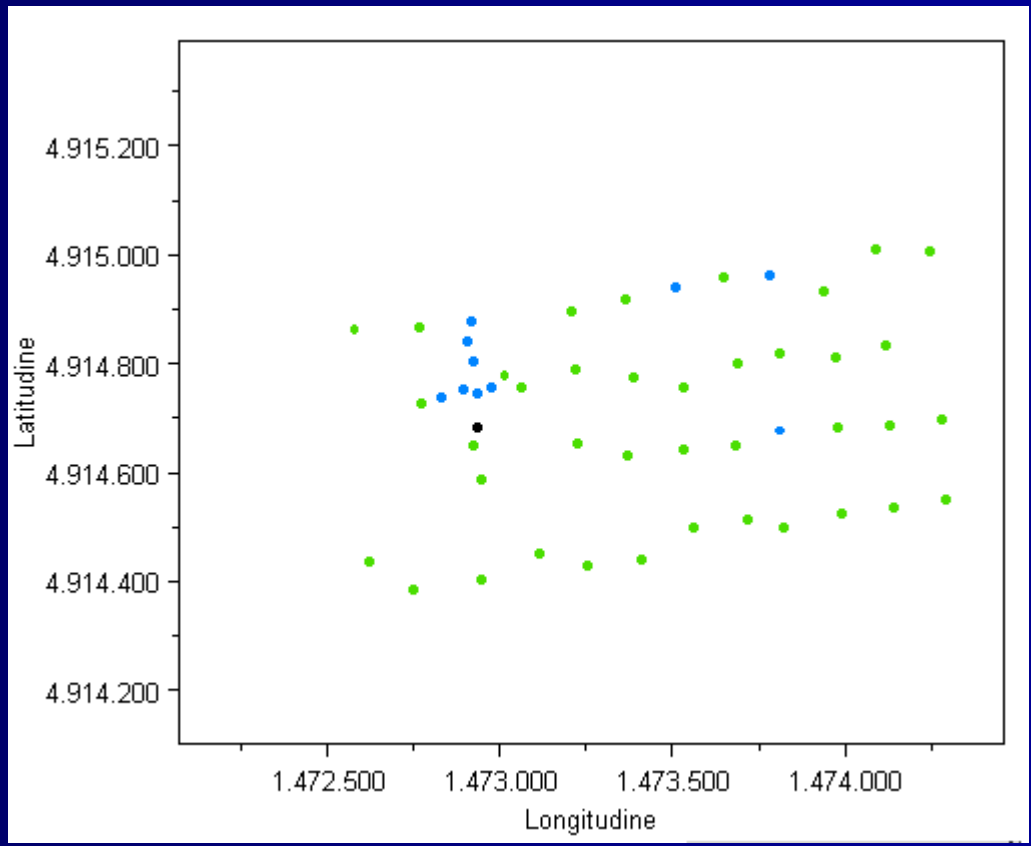
Site characterization / 7
Looking for a natural Cr background value



Quantile-quantile graphic

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

Site characterization / 8
Looking for a natural Cr tot background value

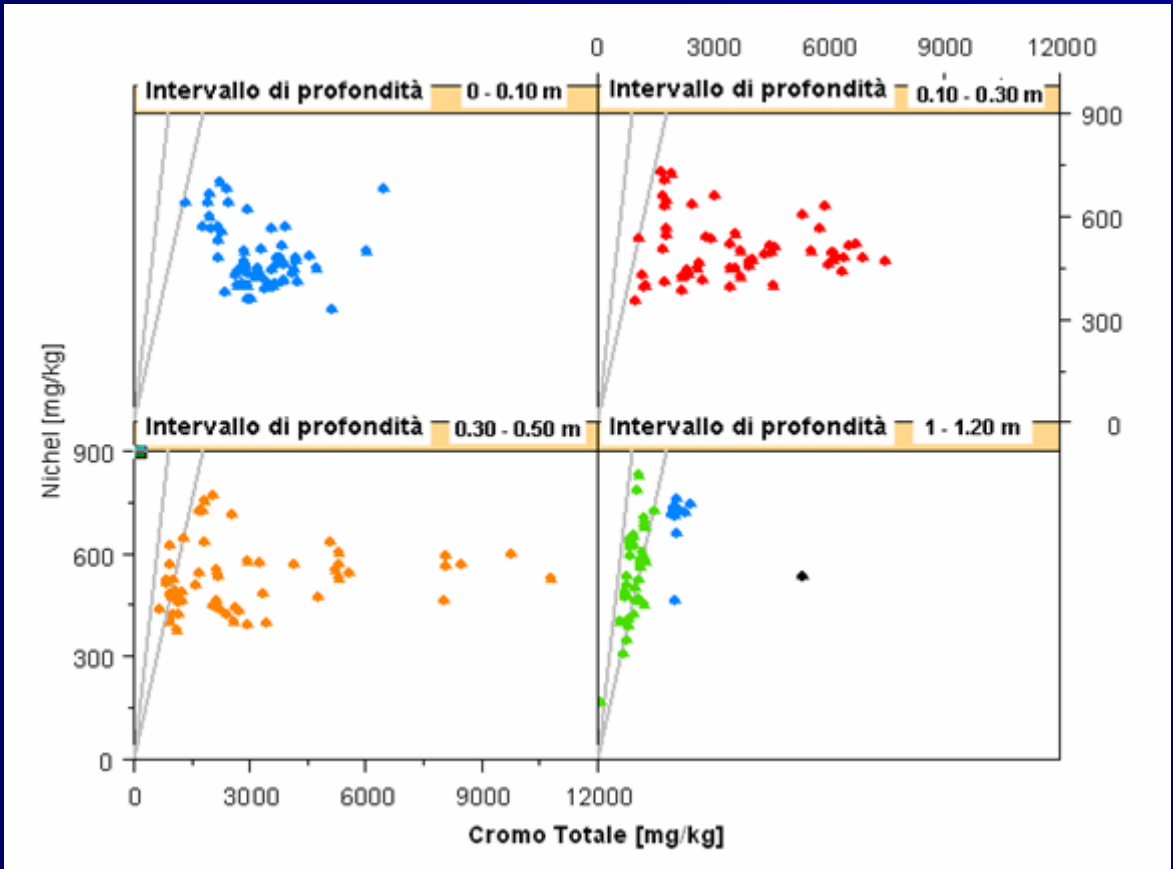


Spatial distibution of Cr tot in the deepest anayzed layer (> 1m deep)

ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

Site characterization / 9
Looking for a natural Cr background value



Cr/Ni ratio at various depths

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

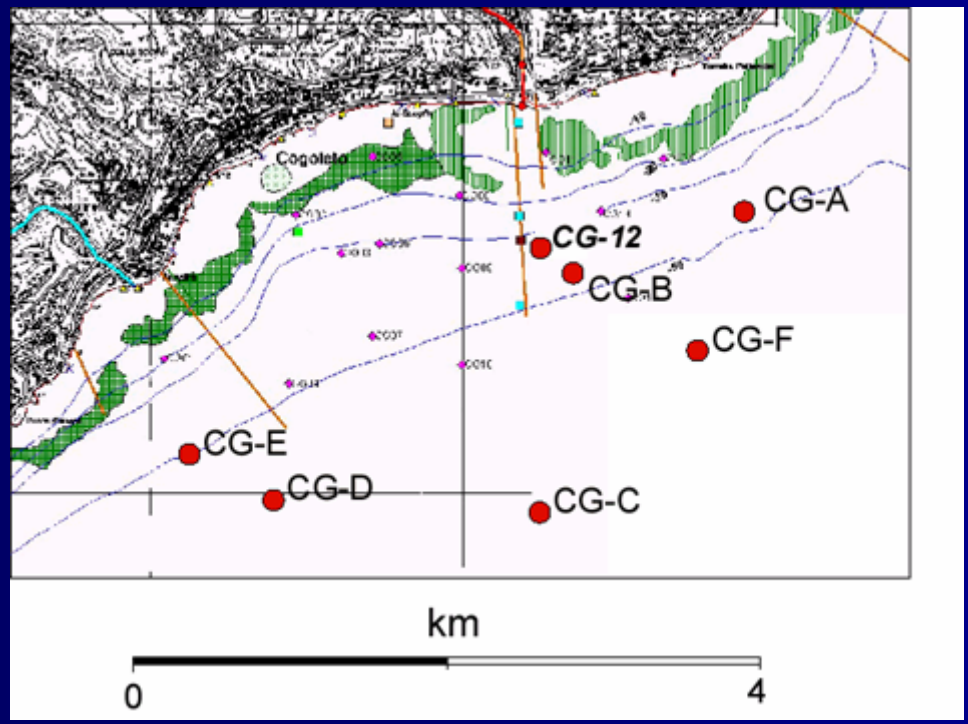
Site characterization / 10
Looking for a natural Cr background value

- Cr/Ni ratio is between 1 and 2 in soils and rocks of this area (and in stream sediments)
- In marine sediment samples, Cr/Ni ratio is much higher (up to 7) in surficial and sub- surficial layers
- In the 100-120 cm layer most of the samples show a "natural" ratio
- Calculation of 95th percentile, with a confidence range of 90%, assuming normal distribution : 1350 ± 100 mg/kg

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

ISMAR Istituto di Scienze Marine
Consiglio Nazionale delle Ricerche

Complementary study/1



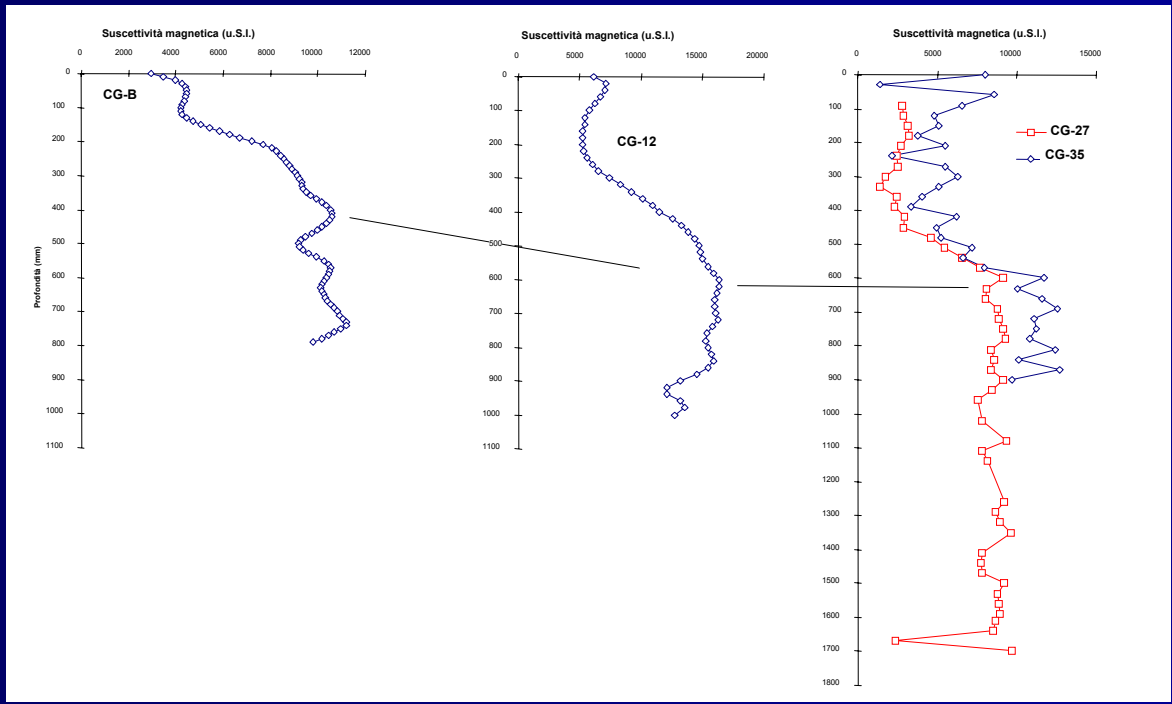
Complementary study sampling points

- 7 sediment cores
- Gravity corer, specially designed to preserve undisturbed top
- Slices 1-4 cm thick, higher resolution near the top
- Chemical analyses : Metals, PAHs, CHN
- Grain size, mineralogy, whole-core magnetic susceptibility
- Radiometric analyses : ^{210}Pb , ^{137}Cs

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

ISMAR Istituto di Scienze Marine
Consiglio Nazionale delle Ricerche

Complementary study/2 magnetic susceptibility



Magnetic susceptibility profiles for CG-B and CG-12 cores
(in comparison with two cores sampled in 2004 by ICRAM during the characterization study- CG 27 and CG-35, right)

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

ISMAR Istituto di Scienze Marine
Consiglio Nazionale delle Ricerche

Complementary study/3 magnetic susceptibility

Maximum magnetic susceptibility:

- in CG-12 at 60 cm depth, like in CG-27 and CG-35 cores
- in CG-B at 40 cm depth
- in CG-A, CG-C, CG-D at 15-20 cm depth
- Sedimentation rate is higher near the river mouth than offshore
- Radiometric analyses have been used to evaluate sedimentation rate

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

ISMAR Istituto di Scienze Marine
Consiglio Nazionale delle Ricerche

Complementary study/4 radiometric analyses

^{210}Pb ($t_{1/2}$ = 22,3 years) and ^{137}Cs ($t_{1/2}$ 30,1 years) can be used to calculate :

- Sediment accumulation rates
- Mass accumulation rates
- Chronologies

In our cores, ^{137}Cs was scarce -> was not possible to recognize the two events typically present in ^{137}Cs depth profiles:

1963 maximum intensity of nuclear atmospheric tests

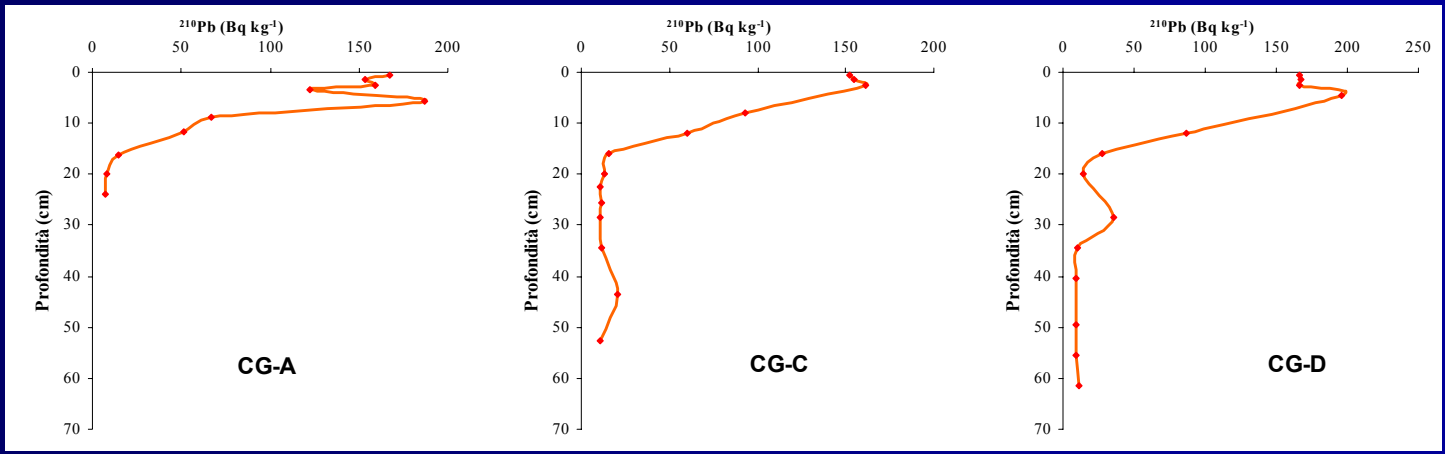
1986 Chernobyl accident

^{210}Pb shows more significant depth profiles

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

ISMAR Istituto di Scienze Marine
Consiglio Nazionale delle Ricerche

Complementary study/5 radiometric analyses



Profiles for ^{210}Pb in CG-A, CG-C, CG-D cores

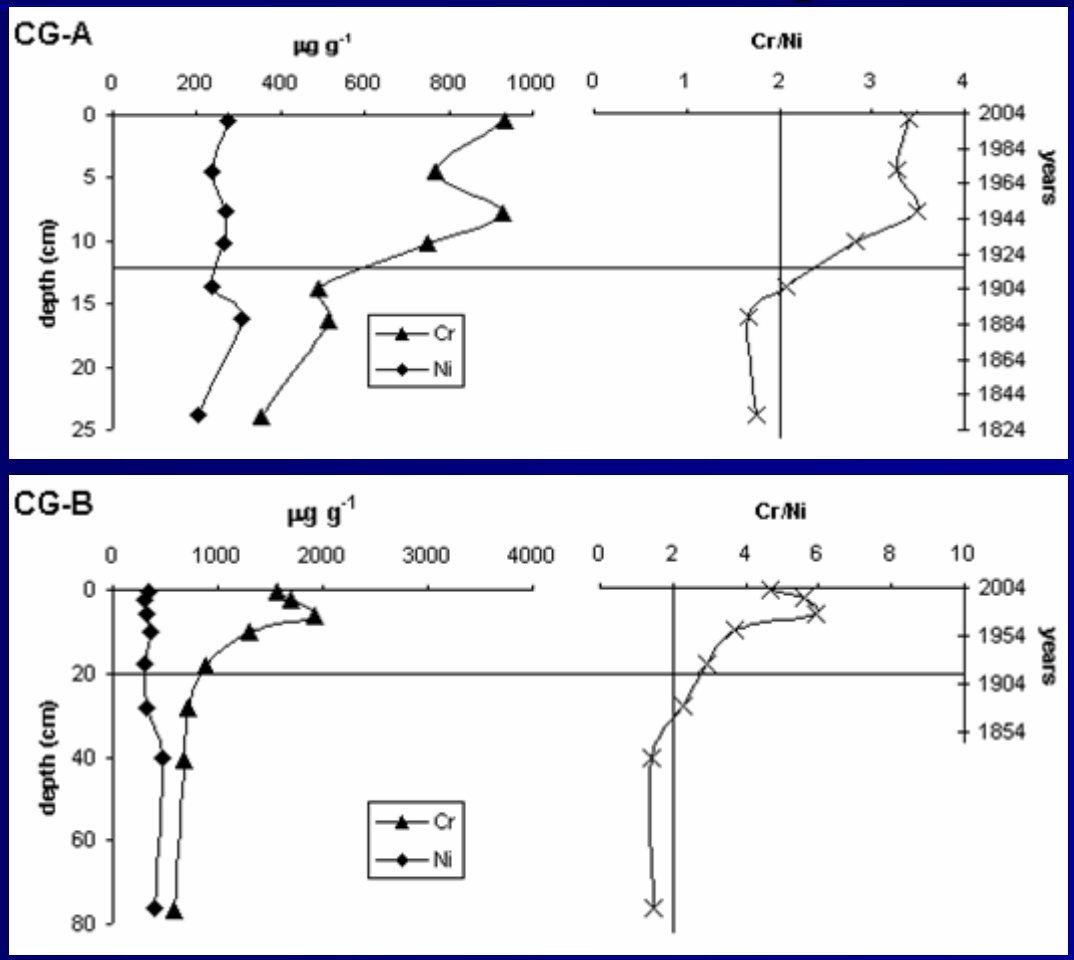
- All ^{210}Pb profiles show constant values from 20 cm depth on (background value)
- Sedimentation rates were calculated using a CF-CS model (constant flux-constant sedimentation) :

0.15-0.20 cm/year for CG-A, CG-C, CG-D
0.6-0,7 cm/year for CG-12

ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

Complementary study/6
determination of Cr natural background value

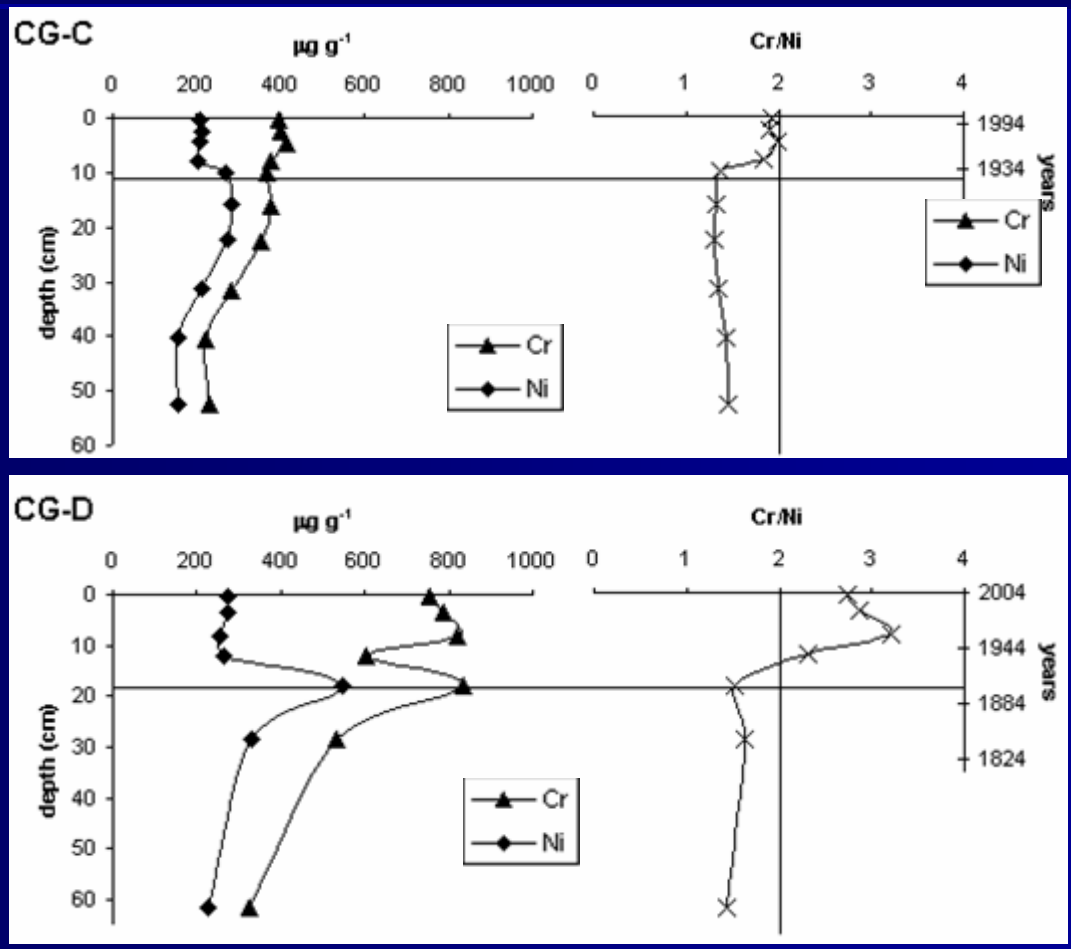


Cr, Ni and Cr/Ni profiles vs. depth and time

ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

Complementary study/7 determination of Cr natural background value

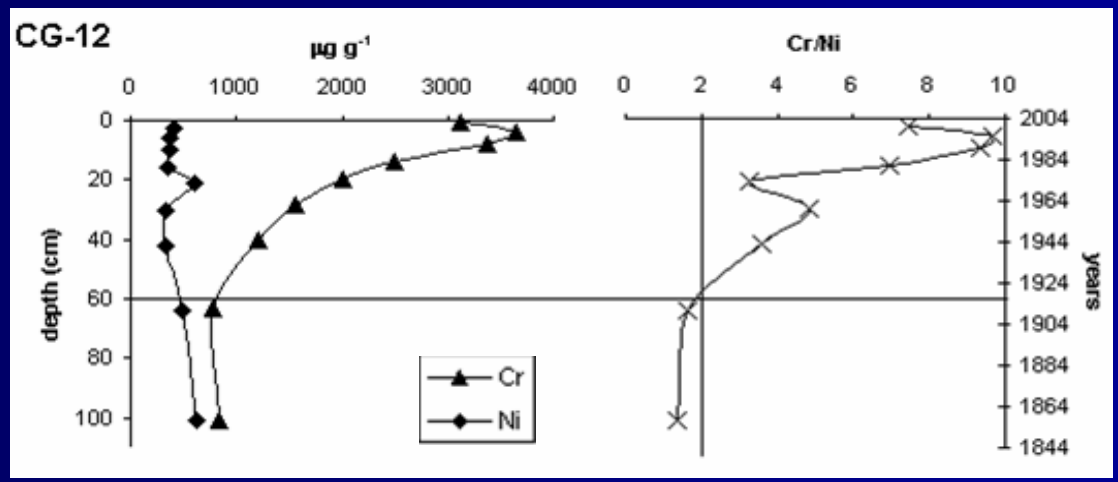


Cr, Ni and Cr/Ni profiles vs. depth and time

ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

Complementary study/8 determination of Cr natural background value



Cr, Ni and Cr/Ni profiles vs. depth and time

- In all cores Cr/Ni ratio is very high at the surface and decreases in deeper layers – that is in older sediments.
- In the layers corresponding to the first decades of last century it is always between 1 and 2 ("natural ratio")
- The depth varies depending on sedimentation rate

ARPAL
Agenzia Regionale per la Protezione dell'Ambiente Ligure

ISMAR Istituto di Scienze Marine
Consiglio Nazionale delle Ricerche

Conclusions

More cores = more information

???

More cores = more money !

High-resolution cores = High degree of information

A small number of high-resolution cores
can significantly reduce the need for a high number of cores

COSTS ARE LOWER

LESS TIME-CONSUMING JOB

ARPAL

Agenzia Regionale per la Protezione dell'Ambiente Ligure

ISMAR Istituto di Scienze Marine

Consiglio Nazionale delle Ricerche

SedNet