Engineering Optimization / Validation of an *In Situ* Reactive Cap for TPH, PCB and Hg-Impacted Sediment Site in Southern Coastal Europe

2019 Battelle Sediments Conference

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Presentation outline

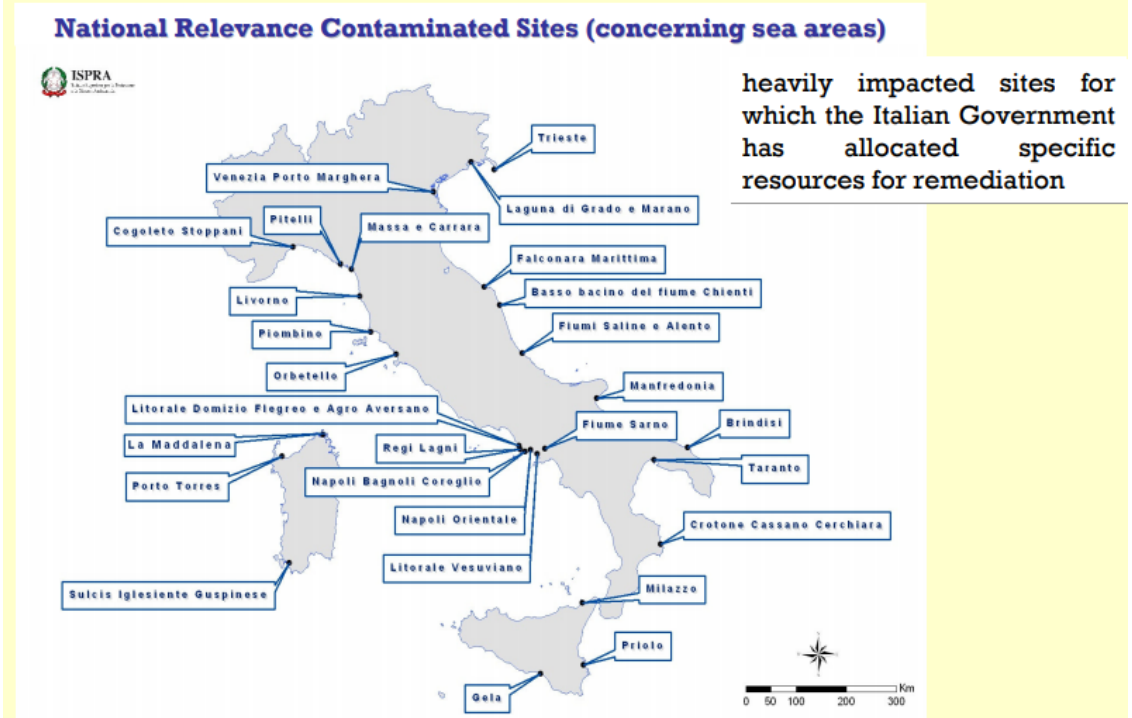
- Background
- *In Situ* Treatments Technologies Considered
- AquaGate® Technologies
  - Core AquaBlok®
  - Reactive AquaGate™ Materials
- Engineering Optimization Testing
  - Materials and methods
  - Results
- Conclusions

Nature of the Problem

- Italy has over 7,600 km of coastline (Greece has over 13,600 km), much of it industrial. [Florida 2,170 km]
- A majority of the industrial operations are along coastlines.
- Contaminated sediments are of environmental concern, and remediation of these sites has proven to be a significant challenge.

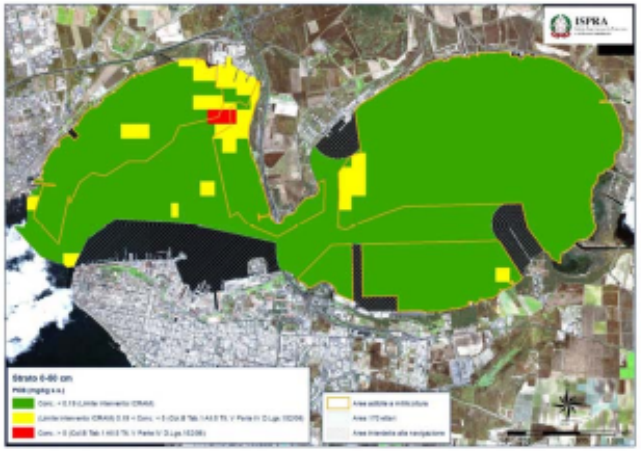
Contaminated Sediments in Italy

- Italy has the greatest amount of contaminated sediments in Europe (estimated >140,000 hectares) and dredges >30 M3 annually
- U.S. Navy has >200 sediment sites.



- The costs associated the sediment cleanup are high: $10M to > $100 M USD per site
- **The costs and magnitude of contaminated sediments in Italy encourage the development of green and sustainable management approaches.**

PCB Sediment Impacts

PCB	Legend: < 0.19 mg/kg; 0.19 < conc. < 5 mg/kg; > 5 mg/kg
 0.0-0.5 m below the seafloor	 0.5-1.0 m below the seafloor
 1.0-1.5 m below the seafloor	 1.5-2.0 m below the seafloor

TPH Sediment Impacts

Total hydrocarbons

Legend: 1000 mg/kg | > 1000 mg/kg

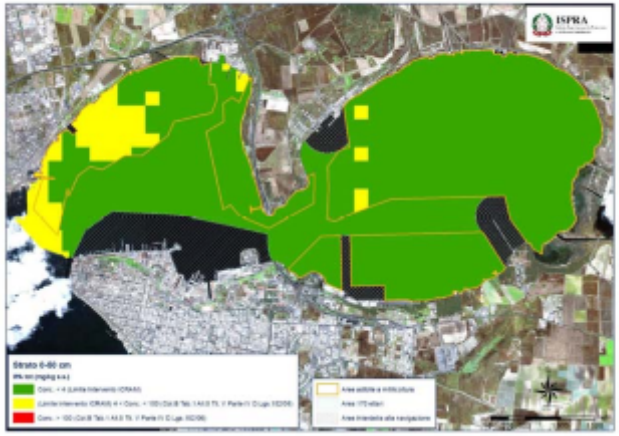
0.0-0.5 m below the seafloor

0.5-1.0 m below the seafloor

1.0-1.5 m below the seafloor

1.5-2.0 m below the seafloor

PAH Sediment Impacts

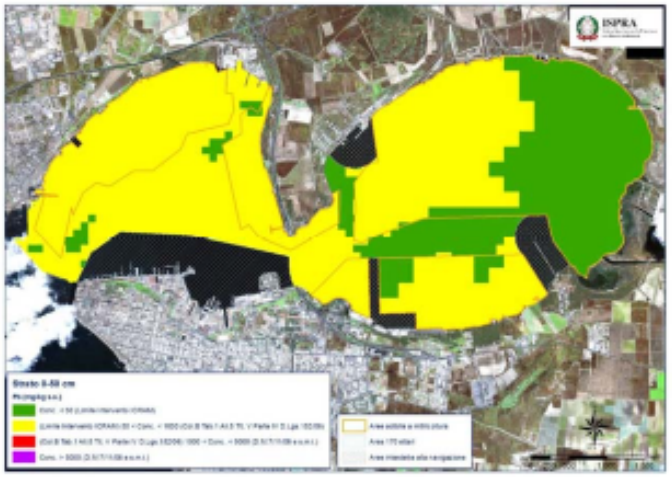
PAH	Legend: < 4 mg/kg; 4 < conc. < 100 mg/kg; > 100 mg/kg
 0.0-0.5 m below the seafloor	 0.5-1.0 m below the seafloor
 1.0-1.5 m below the seafloor	 1.5-2.0 m below the seafloor

Pb Sediment Impacts

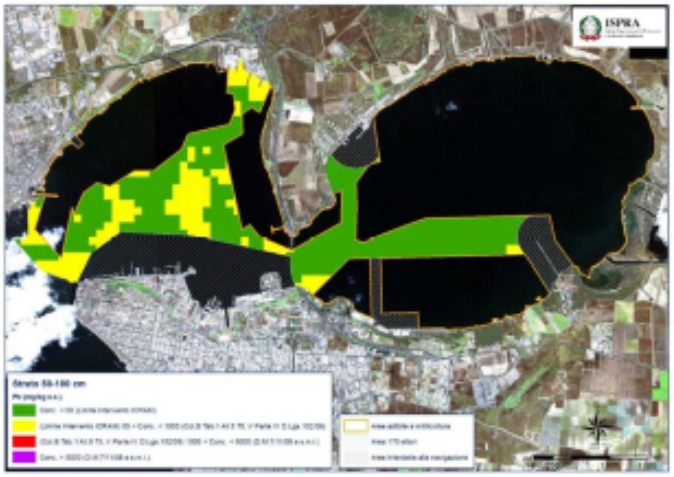
Lead

Legend

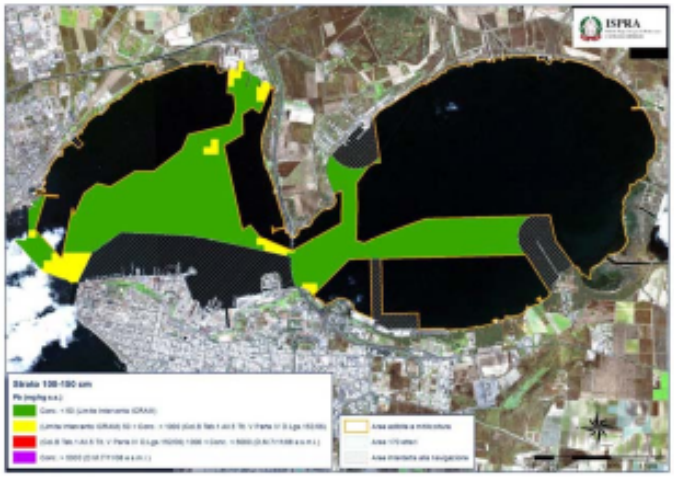
< 50 mg/kg | 50 < conc. < 1000 mg/kg | > 1000 mg/kg



0.0-0.5 m below the seafloor



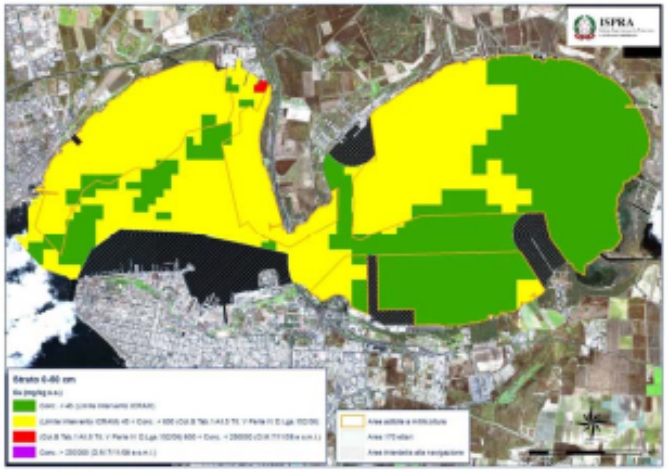
0.5-1.0 m below the seafloor



1.0-1.5 m below the seafloor

1.5-2.0 m below the seafloor

Cu Sediment Impacts

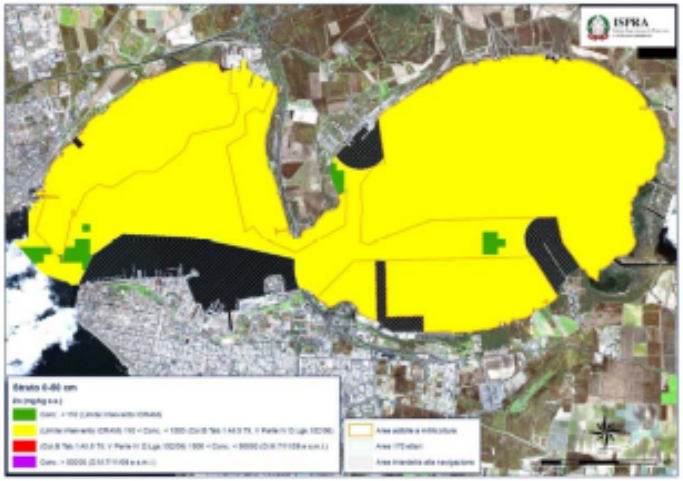
Copper	Legend: < 45 mg/kg; 45 < conc. < 600 mg/kg; > 600 mg/kg
 0.0-0.5 m below the seafloor	 0.5-1.0 m below the seafloor
 1.0-1.5 m below the seafloor	 1.5-2.0 m below the seafloor

Zn Sediment Impacts

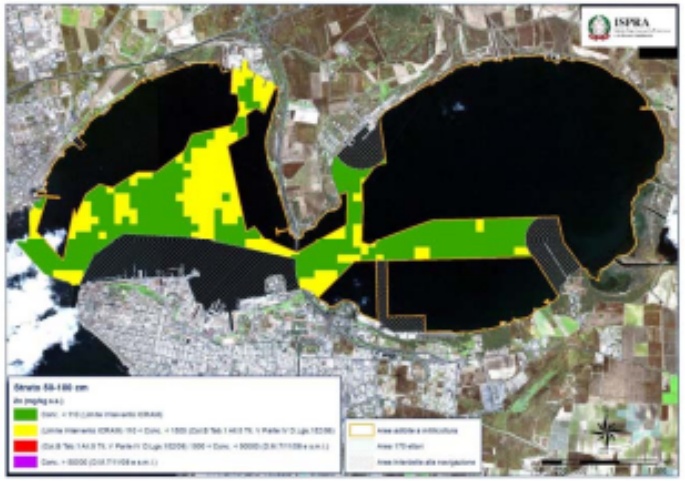
Zinc

Legend

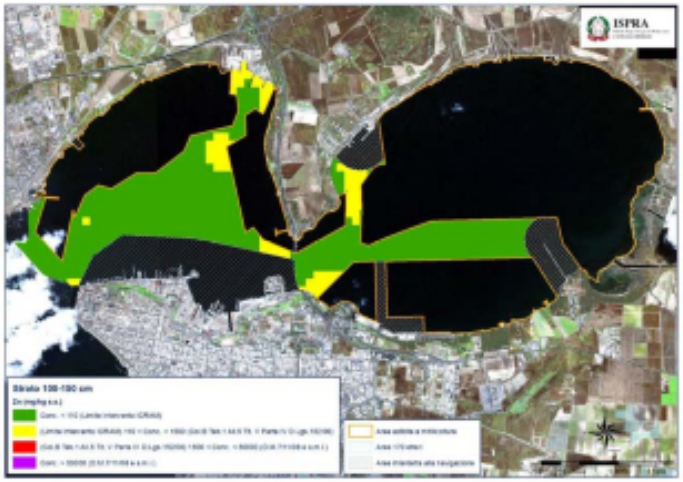
< 110 mg/kg | 110 < c < 1500 mg/kg | > 1500 mg/kg



0.0-0.5 m below the seafloor



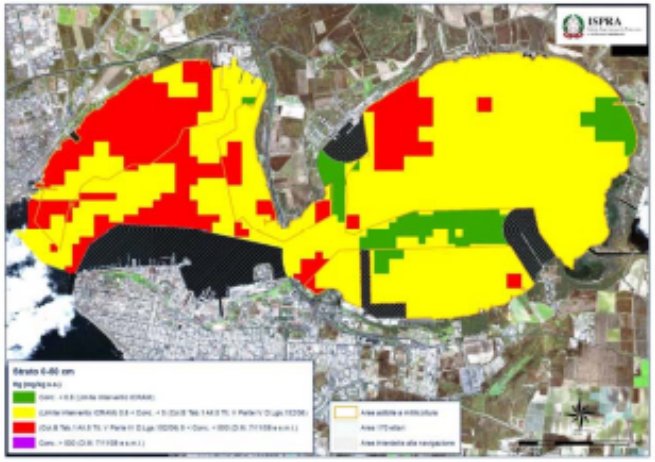
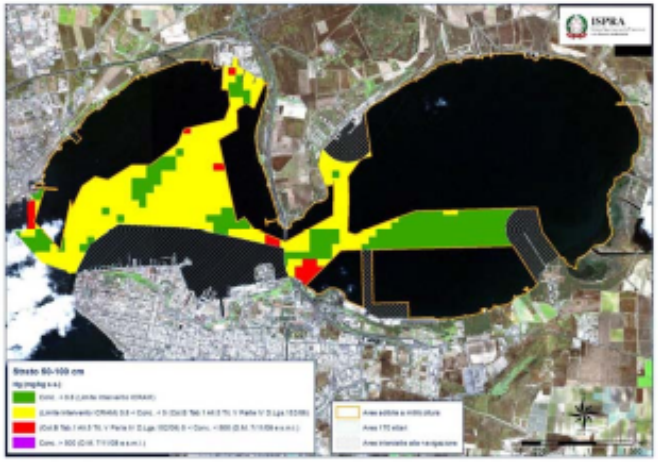
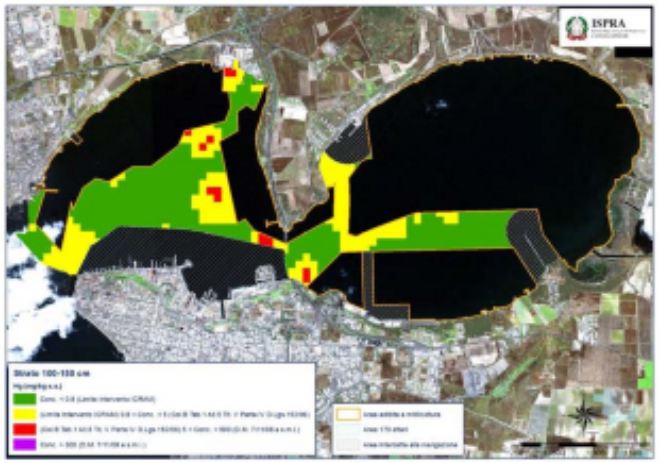
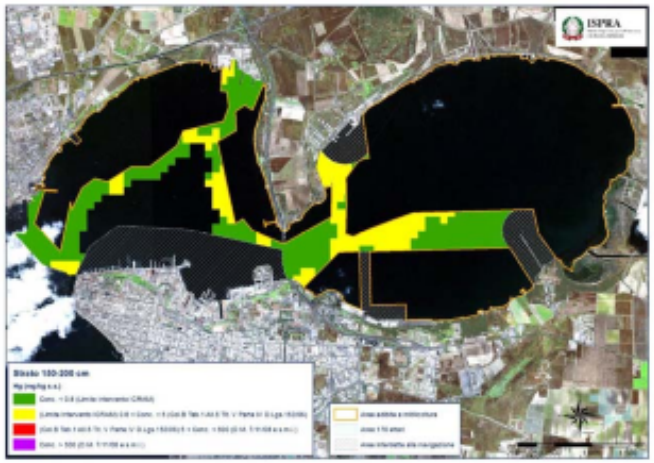
0.5-1.0 m below the seafloor



1.0-1.5 m below the seafloor

1.5-2.0 m below the seafloor

Hg Sediment Impacts

Mercury	Legend: < 0.8 mg/kg; 0.8 < conc. < 5 mg/kg; > 5 mg/kg
	
0.0-0.5 m below the seafloor	0.5-1.0 m below the seafloor
	
1.0-1.5 m below the seafloor	1.5-2.0 m below the seafloor

Remedial Options

I Bonifica e riqualificazione ambientale delle sponde e delle aree contigue

II Rimozione sostenibile e smaltimento dei materiali di natura antropica dal fondale

III Bonifica degli ordigni e dei residuati bellici

IV Interventi per la mitigazione degli impatti derivanti dagli scarichi

V Interventi per l'abbattimento delle fonti di contaminazione provenienti dalla rete idrografica superficiale

VI Interventi per l'abbattimento delle fonti di contaminazione da deflusso delle acque sotterranee

VII Interventi di bonifica e/o messa in sicurezza dei sedimenti

VIII Tutela, monitoraggio e traslocazione di specie di interesse conservazionistico

IX Rimozione mercato ittico galleggiante

Figura 43 - Aree d'intervento nel I Seno del Mar Piccolo

Various remedial approaches considered:

- Dredging and Storage or Disposal
- Natural Attenuation
- Capping

In Situ Capping Technologies

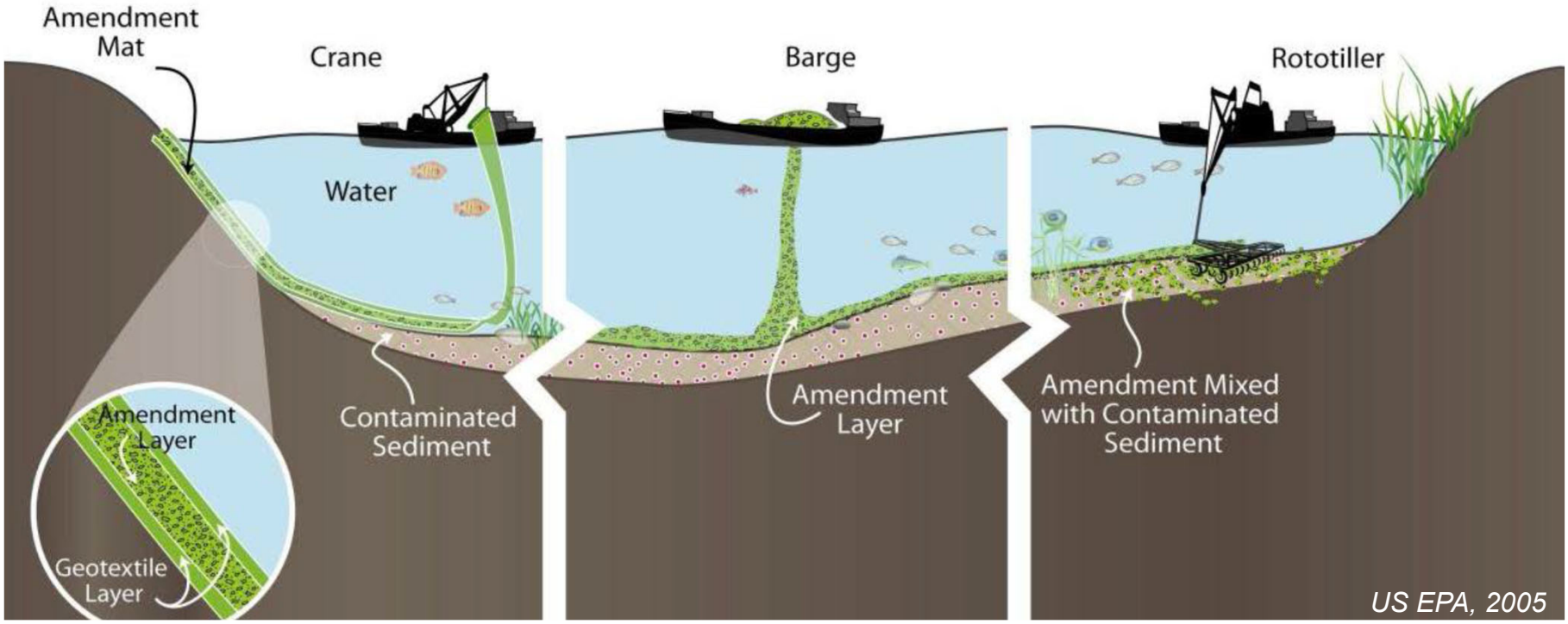
In situ capping is an internationally accepted technology for hazardous chemical site remediation. Capping offers several advantages with less limitations compared to other remediation technologies (i.e. dredging, natural recovery).

Two general approaches are possible:

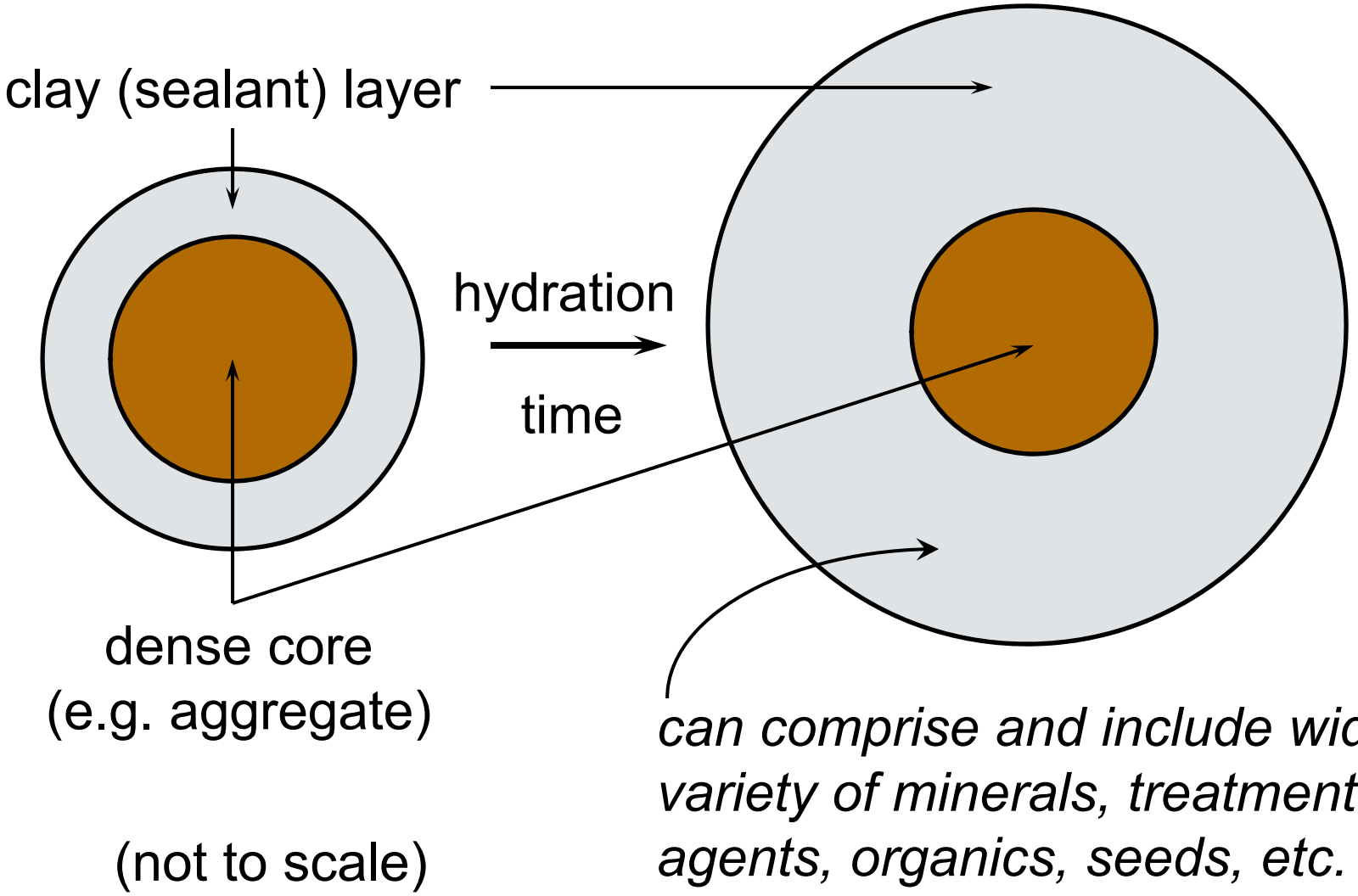
1. **passive capping**, which is the deployment of a barrier of material that is relatively impermeable to both the water above and the contaminants below;
2. **active/reactive capping**, which exposes contaminants to one or more additives or amendments, addressing contaminants as they migrate through the treated area

Delivery of *In Situ* Treatments Technologies

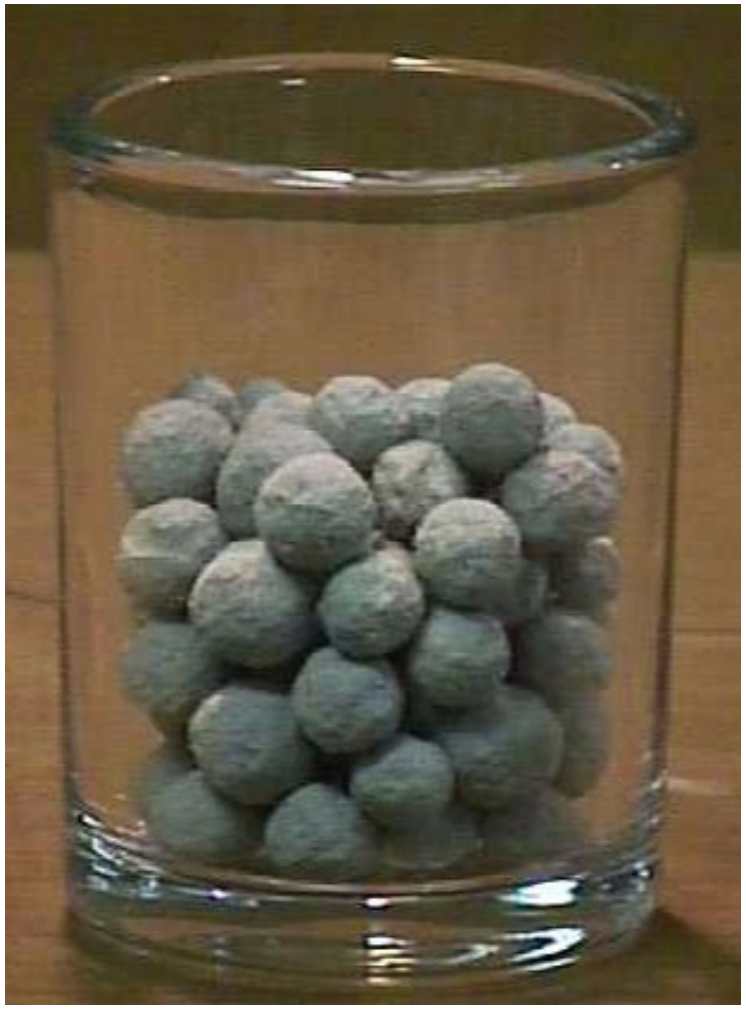
Amendments can be contained in a mat, applied in bulk onto the sediment surface, mixed in the sediment, added as part of a sand cap, or as a layer within a sand cap.



Or… Using AquaBlok *In Situ* Capping Technology



Basic Product Behavior in Water



AquaBlok Placement Methods

Recontamination is Not Due to Flux Through the Cap

Split-core from Section A (2.5 yrs after placement)

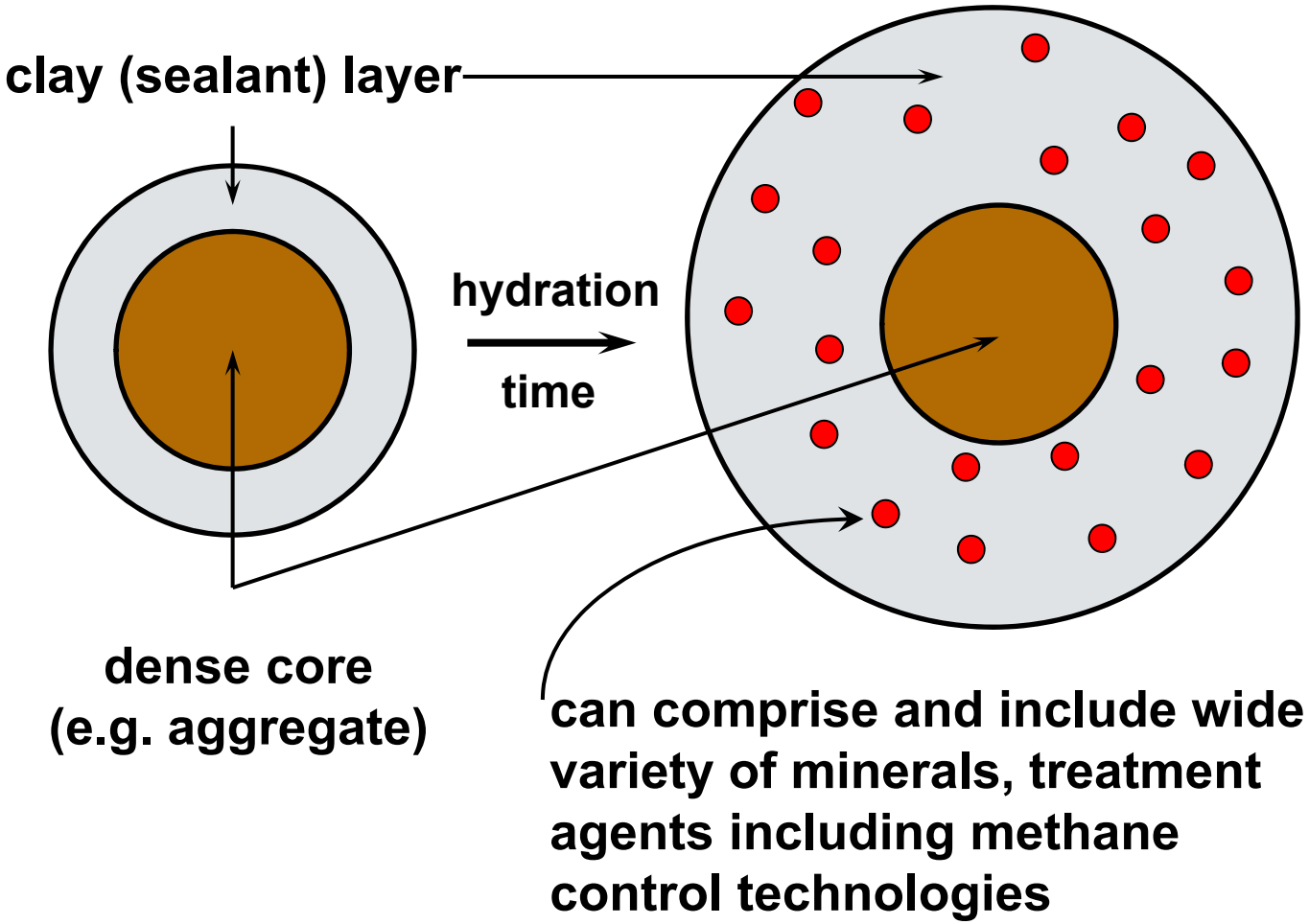
New sediment Deposits

AquaBlok Clean Cap Layer

Discrete boundary

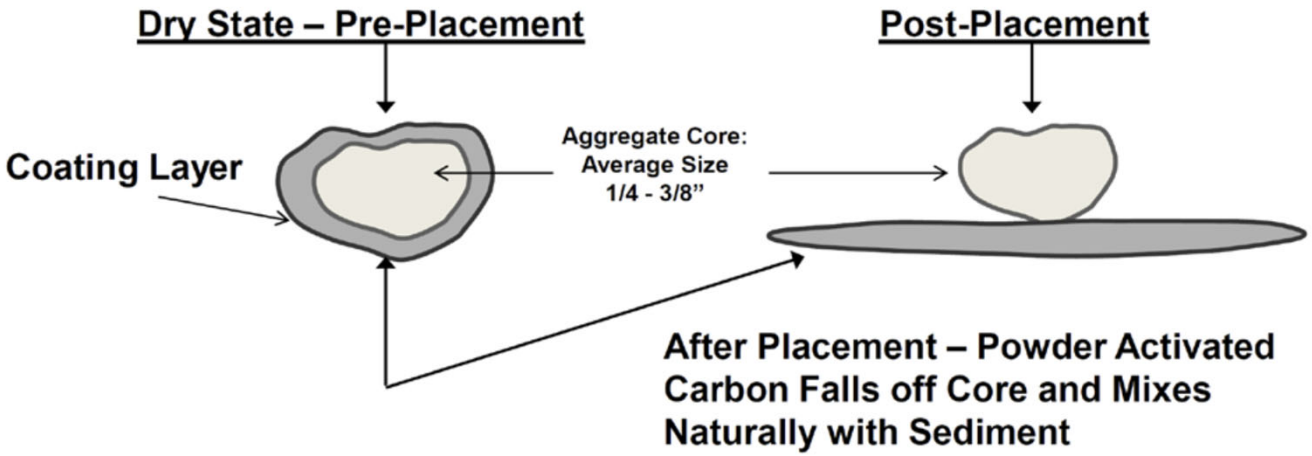
Contaminated Sediment

AquaGate® as a Delivery Vehicle for Reactive Amendments



Reactive AquaGate®

AquaGate® are patented materials consisting of AquaBlok® aggregate core covered by a clay or clay-sized materials, and polymer coating.



The aggregate core can be supplemented with:

- Organoclay
- Provect-IRM™
- Iron oxide
- Zero valent iron (ZVI)
- Aluminum sulfate
- Activated carbon (PAC)
- Microbes
- Provect-ORS™
- Others

AquaGate® + PAC

- AquaGate®+PAC (Powdered Activated Carbon) is a patented, composite-aggregate technology resembling small stones typically comprised of a dense aggregate core, clay or clay-sized materials, polymers, and fine grained activated carbon additives.

Specification

Aggregate:	Nominal AASHTO #8 (1/4-3/8”) or customized to project-specific need
Activated Carbon:	Powdered – Iodine Number 800 mg/ 99% (minimum) through 100 mesh sieve 95% (minimum) through 200 mesh sieve 90% (minimum) through 325 mesh sieve Typically 2 – 5% by weight
Binder:	Cellulosic polymer
Permeability:	1 x 10-1 to 1 x 10-2 cm/sec
Dry Bulk Density:	85 – 90 lbs/ft3

AquaGate® + Provect-IRM®

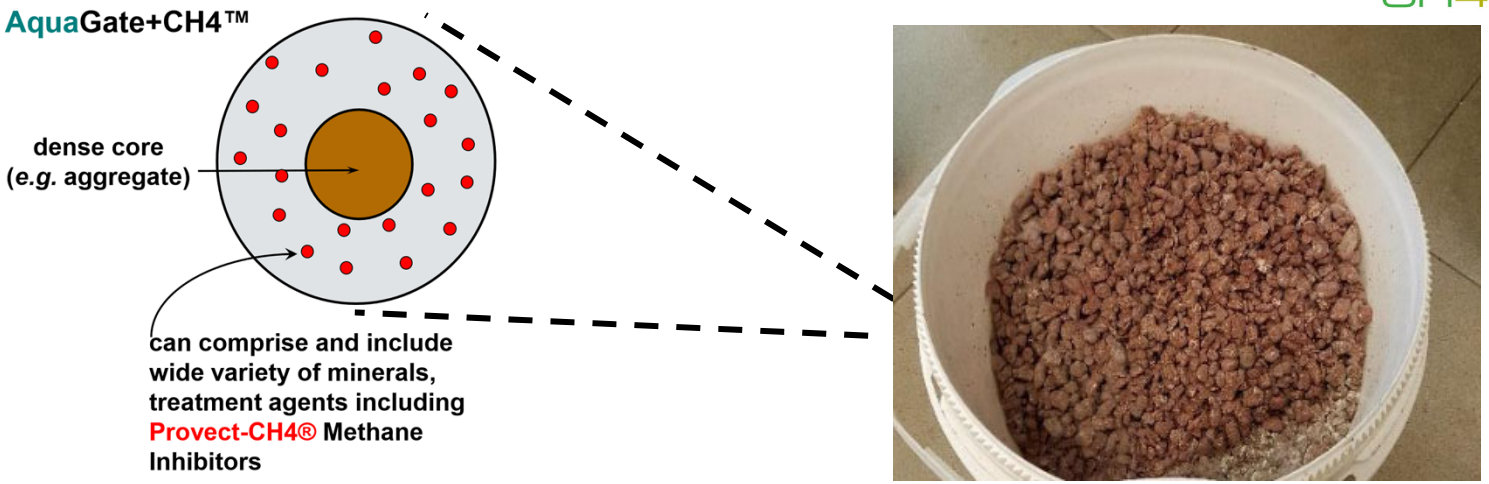
- AquaGate®+IRM integrates a powdered reagent for metals stabilization at ca. 1% to 5% total weight. Can also reduce some organic contaminants to less toxic by-products.

Product Specifications

Aggregate:	Nominal AASHTO #8 (1/4-3/8") or custom-sized to meet project-specific need * Limestone or non-calcareous substitute, as deemed project-appropriate
Sorbster:	Powdered – Approximate 200 Mesh ◦ Rust/Orange Powder; Odorless Manufacturers – Product Designation ◦ MAR Systems, Inc. – Sorbster ** Formulations Range from 2-5% by weight*
Mercury Binding:	Chemsorptive process – 50-100% removal in batch treatability testing
Permeability:	1×10^{-2} to 1×10^{-5} cm/sec
Dry Bulk Density:	75 – 85 lbs/ft^3
Moisture:	10 – 20% (maximum)

AquaGate® + Provect-CH4®

- Provect-CH4® methanogen inhibitors have been combined with AquaGate® to yield a composite particle containing an aggregate core that is layered with the reactive amendment materials and deployed through a water column over a contaminated site.
- In the AquaGate® approach, Provect-CH4® is introduced in an initial application before placing the AquaBlok® sequestration cap to **inhibit Hg methylation after cap placement**.



Case Study

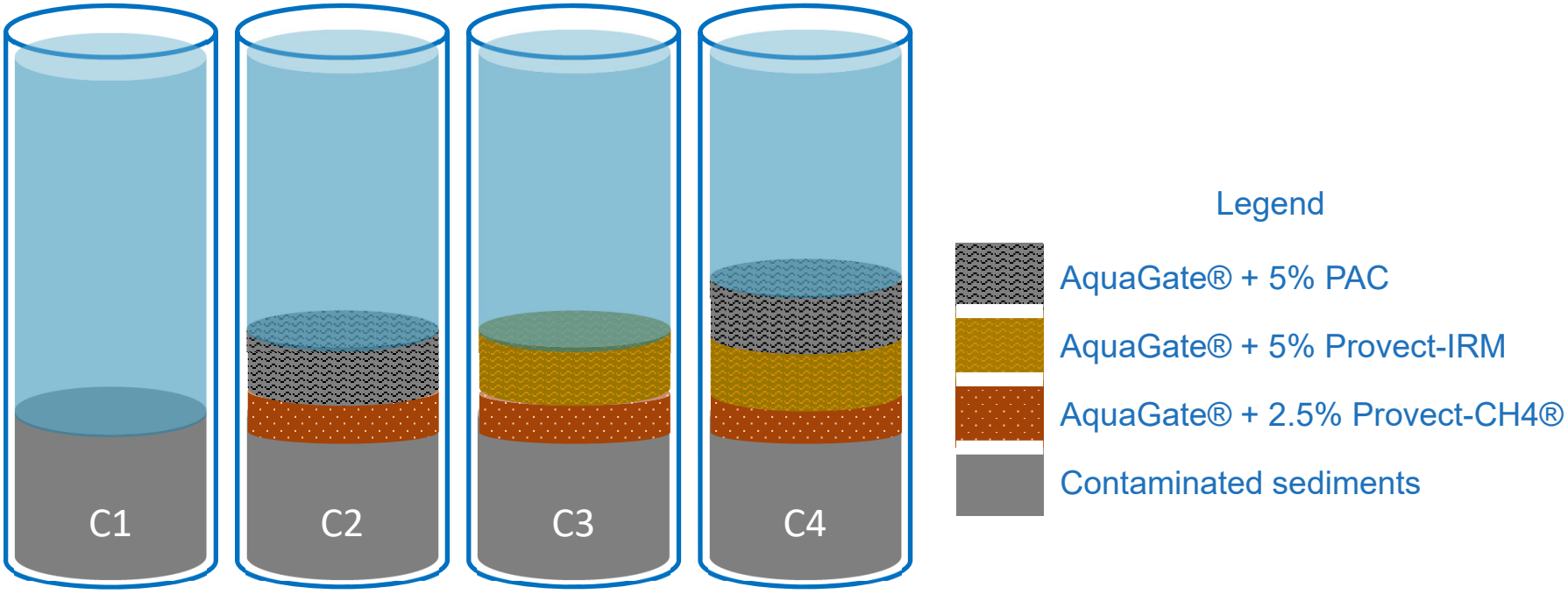
Marine sediments at an industrial site in southern Europe are impacted by elevated concentrations of petroleum hydrocarbons, PCBs, and mercury (along with other heavy metals).

Contaminants	Unit	Value	Law limit
Hg	mg/kg ss	2.5	0.80
Pb	mg/kg ss	95.5	50
Cu	mg/kg ss	60.5	45
Zn	mg/kg ss	175	110
PAHs	µg/kg ss	6,100	4,000
PCBs	µg/kg ss	1,850	190

Sediments are essentially fine-grained soils, for which the clay fraction is 40%, silt fraction 45% and sand fraction 15%.

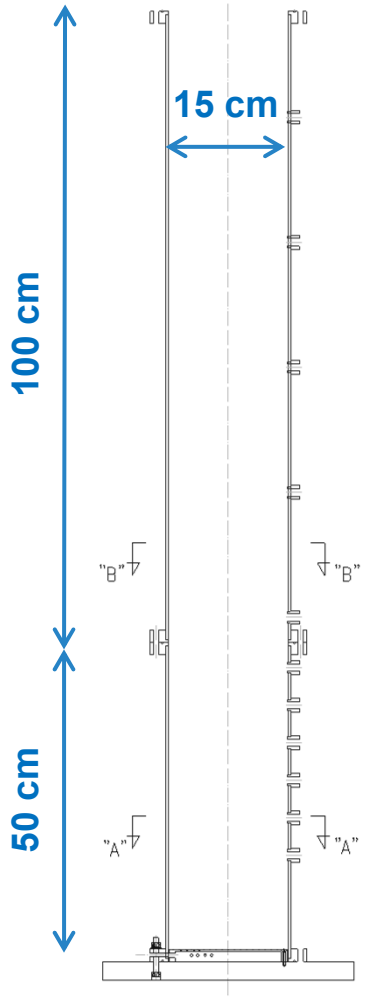
Case Study

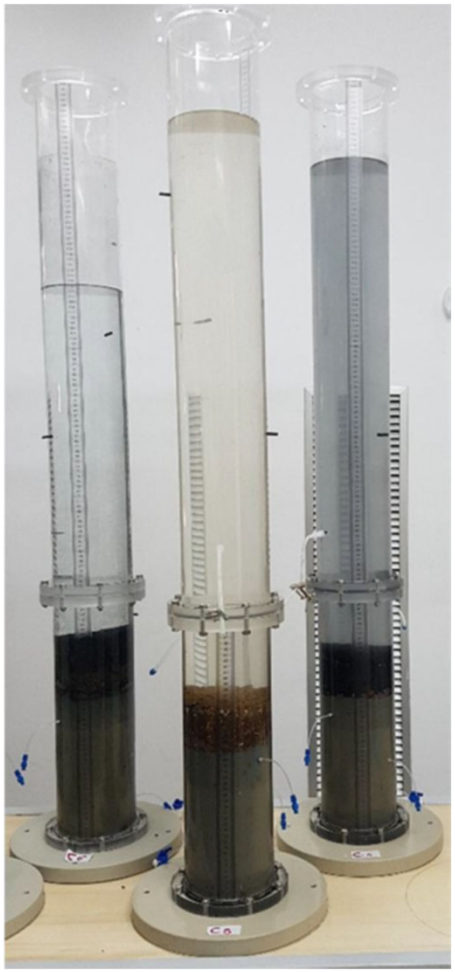
Laboratory tests were conducted to evaluate the effectiveness of various AquaGate® *in situ* capping technologies as a delivery vehicle for various Provectus amendments to yield effective treatment. Columns were prepared with marine sediments and sea water collected from the site



NOT IN SCALE

Laboratory Study





- Intended to model subaqueous contaminated sediment, reactive capping, and water column in place.
- Columns 15 cm in diameter and 150 cm in length..
- Multiport sampling locations at different heights along the columns
- Settlement of the top sediments can be recorded over time to follow the development of the consolidation process.

Results: Heavy Metals in Water Column

/	Unit	C1		C2		C3		C4	
		0 days	20 days	0 days	20 days	0 days	20 days	0 days	20 days
Hg	µg/L	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Pb	µg/L	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	1.0	< 1.0	< 1.0
Cu	µg/L	< 1.0	1.0	< 1.0	< 1.0	< 1.0	1.0	< 1.0	1.0
Zn	µg/L	9.0	60.3	9.0	1.0	9.0	1.0	9.0	< 1.0

Metals were detected in seawater samples, but some of these values were statistically equal to those measured for pre-capping conditions.

The monitoring of columns showed a slight consolidation (i.e. few mm) although no significant flow of metals was observed. The flow of metals has been successfully mitigated by the chemical isolation of capping materials.

EPA 200.8

Metals Data Water Column

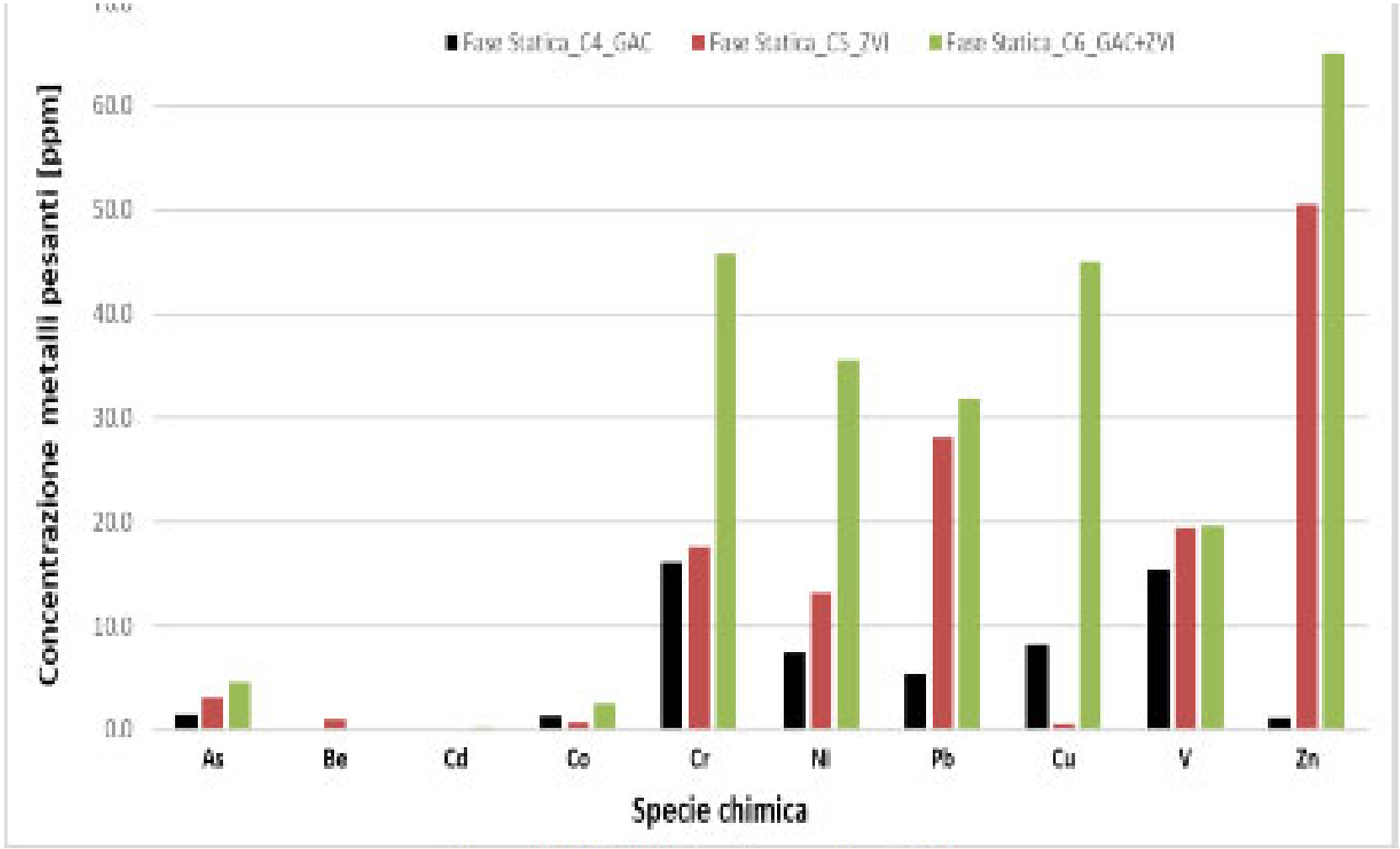
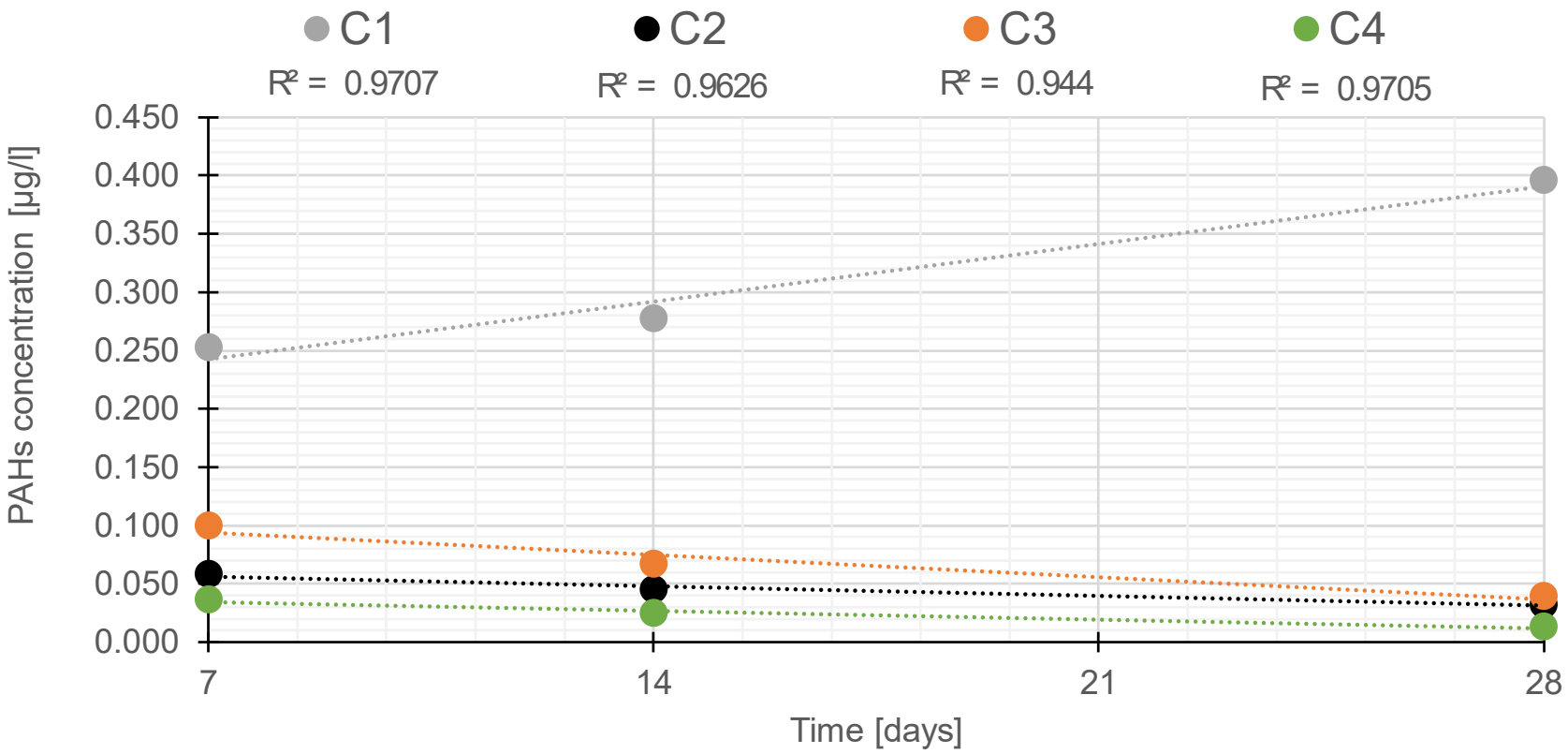


Figura 81- Metalli Pesanti presenti nel CAP

Results:
PAHs in Column Water

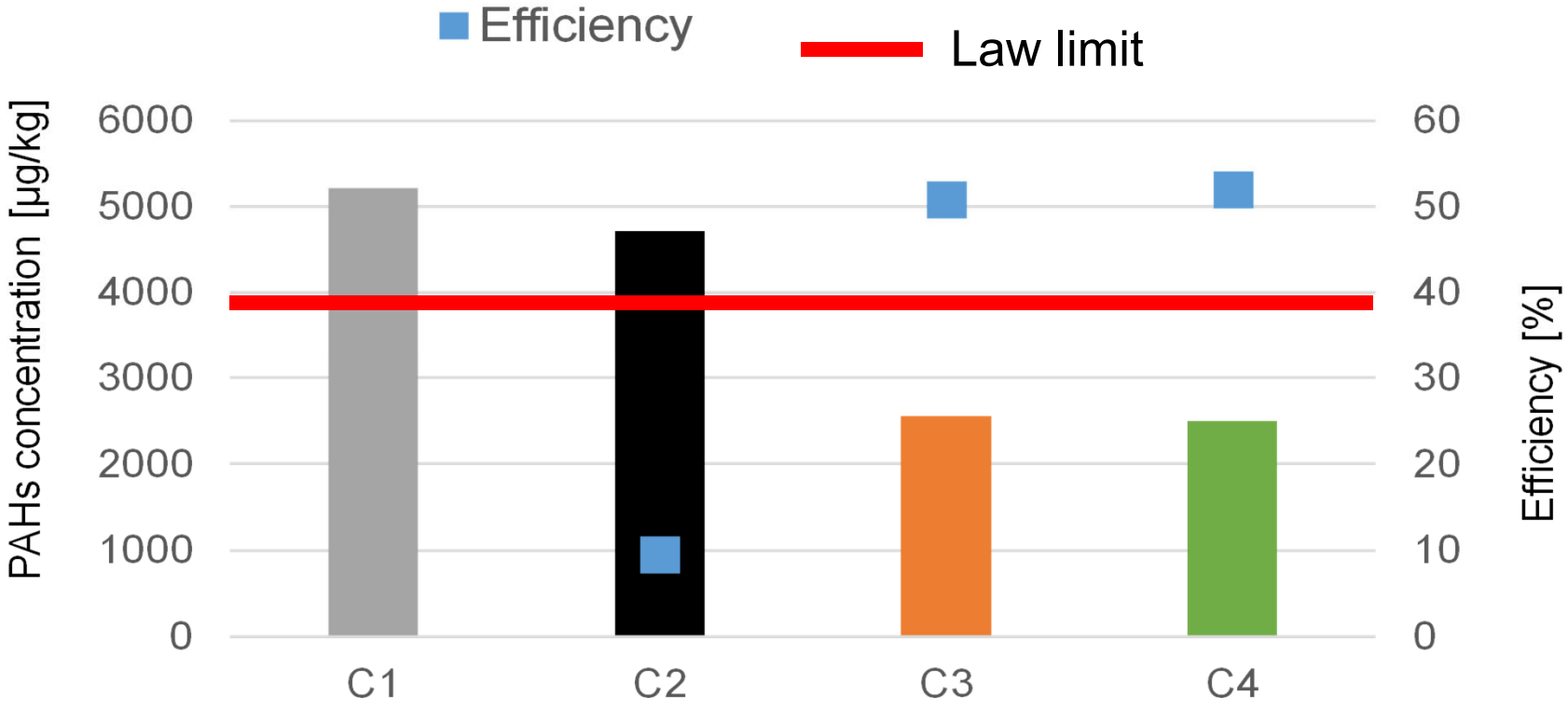


C2 = AquaGate+PAC+Provect-CH4

C3 = AquaGate+Provect-IRM+Provect-CH4

C4 = AquaGate+PAC+Provect-IRM+Provect-CH4

Results:
PAHs in Capped Sediments



C2 = AquaGate+PAC+Provect-CH4

C3 = AquaGate+Provect-IRM+Provect-CH4

C4 = AquaGate+PAC+Provect-IRM+Provect-CH4

EPA 8275A

Results:
PCBs in Water Column

PCBs in seawater samples were not detectable (detection limit is approximately 0.001 µg/L).

After 28 days an apparent reduction of PCBs in the sediment was observed.

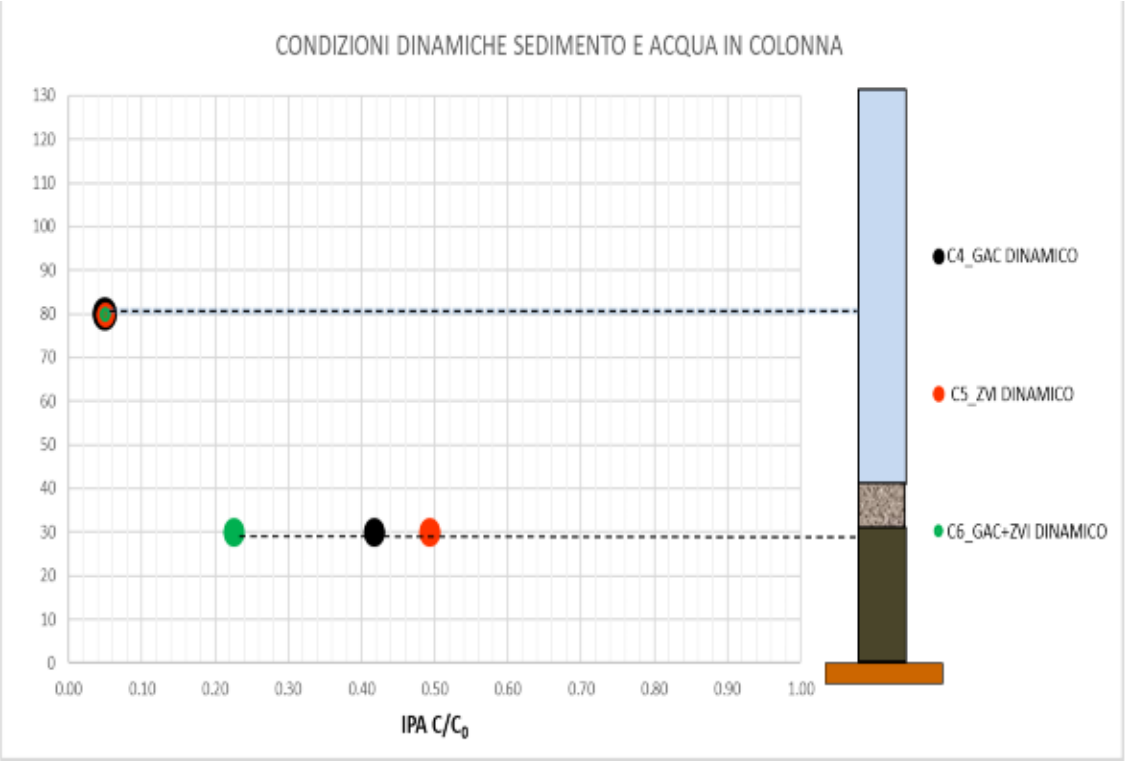
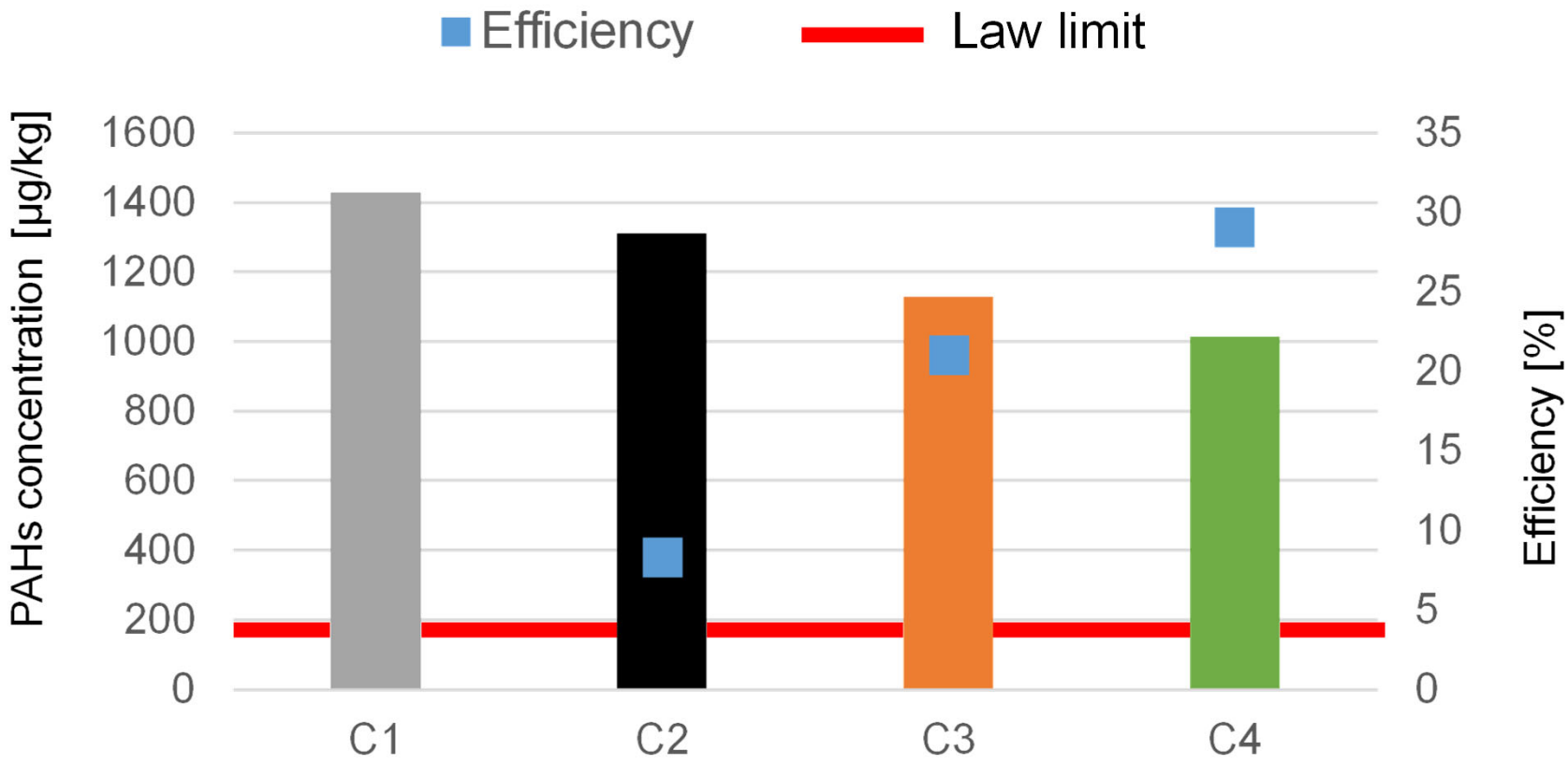


Figura 84 – concentrazione degli IPA nel sedimento e nell'acqua in colonna alla fine della fase dinamica

EPA 8275A

Results:
PCBs in Capped Sediments



C2 = AquaGate+PAC+Provect-CH4

C3 = AquaGate+Provect-IRM+Provect-CH4

C4 = AquaGate+PAC+Provect-IRM+Provect-CH4

EPA 8275A

Conclusion

- Column tests showed that reactive AquaGate® materials represent an effective option for *in situ* remediation of contaminated marine sediments.
- AquaGate® + Provectus supplement performed better than all other technologies and approaches tested.
- Without capping, a gradual increase in the concentrations of PAHs in the water column was observed.
- Field-scale pilot tests are under contract to be further evaluate the reactive capping approach with special reference to the long-term effectiveness of the amendments.

Field Application

- AquaGate® materials applied at 1.5x lab rates:
  - AquaGate®+PAC 5% = 7.5 cm
  - AquaGate®+Provect-IRM 5% = 6.0 cm
  - AquaGate®+Provect-CH4 2.5% = 3.0 cm

- 800 m2 test area will require:
  - AquaGate®+PAC = 91.5 kg/m2 or 73.2 MT
  - AquaGate®+Provect-IRM = 81.8 kg/m2 or 65.4 MT
  - AquaGate®+Provect-CH4 = 40.9 kg/m2 or 32.7 MT

    TOTAL 214.2 kg/m2 or 171.3 MT AquaGate+

- Made in USA $500 to $1,500/MT (for pilot)
- Made locally = estimated 50% less (for full scale)

THANKS FOR THE ATTENTION,

Dr. Jim Mueller

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B A W

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