

HAZRUNOFF

PROJECT

Practical exercise on HNS behaviour SEBC understanding

CEDRE

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Contents

- Explosivity and flammability
- Toxicological threshold values
- Environmental limits
- Example of environmental programme



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Why do we need thresholds limits?

- Cartography: according to modelling forecasts of chemicals dispersal
- Evaluation: giving information to response teams
- Emergency measures: population evacuation, fishing exclusion zone...



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What is a toxicological threshold value?

- Definition: the minimum concentration of a substance that causes a negative effect, that may be of varying severity, on a human population for a given exposure time
- Determining: extrapolation to humans of data obtained from experiments on animals



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What do we need toxicological threshold value?

- To know if intervention is possible
- To evaluate if population need to be confined or evacuated



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Which are the limits of this values?

- No globally harmonized system
- Each type of value has its own definition and was developed in specific purposes



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Immediately Dangerous to Life or Health (IDLH)

- 1994** Maximal concentration in the air until which one worker can escape without risking to die or to feel irreversible effects on the health following severe respiratory or eye irritation and other noxious effects (disorientation or lack of coordination)
- 1987** Maximal concentration in the air until which a person exposed for at most 30 minutes can run away without risk of irreversible effects for the health.




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AEGL values

Concentration of a substance in the air over which...

- 
- 3 ...the potentially **mortal** effects or the **deaths** could arise within the population.
 - 2 ...the **irreversible** effects, the **severe harmful** effects or **long-term opposite** effects could be observed within the population.
 - 1 ...the population could present signs of notable **discomfort** and **irritation** or other signs that are **non-sensory** and **asymptomatic**. These effects are **non-invalidating** and **reversible** after exposure cessation.



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EPRG values

Maximal atmospheric concentration below which...

3

...It is likely that almost all the individuals could be exposed during more than one hour without feeling or developing of effect threatening their life.

2

...it is likely that almost all the individuals could be exposed during more than one hour without feeling or developing irreversible or incapacitating effects.

1

...it is likely that almost all individuals could be exposed more than one hour without feeling more than light passing effects or detecting a smell.



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TEEL values

Concentration limit below which...

3

... it is likely that almost all the individuals could be exposed without feeling or developing effect threatening their life.

2

... it is likely that almost all the individuals could be exposed without feeling or developing irreversible or incapacitating effects.

1

... it is likely that almost all the individuals could be exposed without feeling more than light passing effects or detecting a smell.

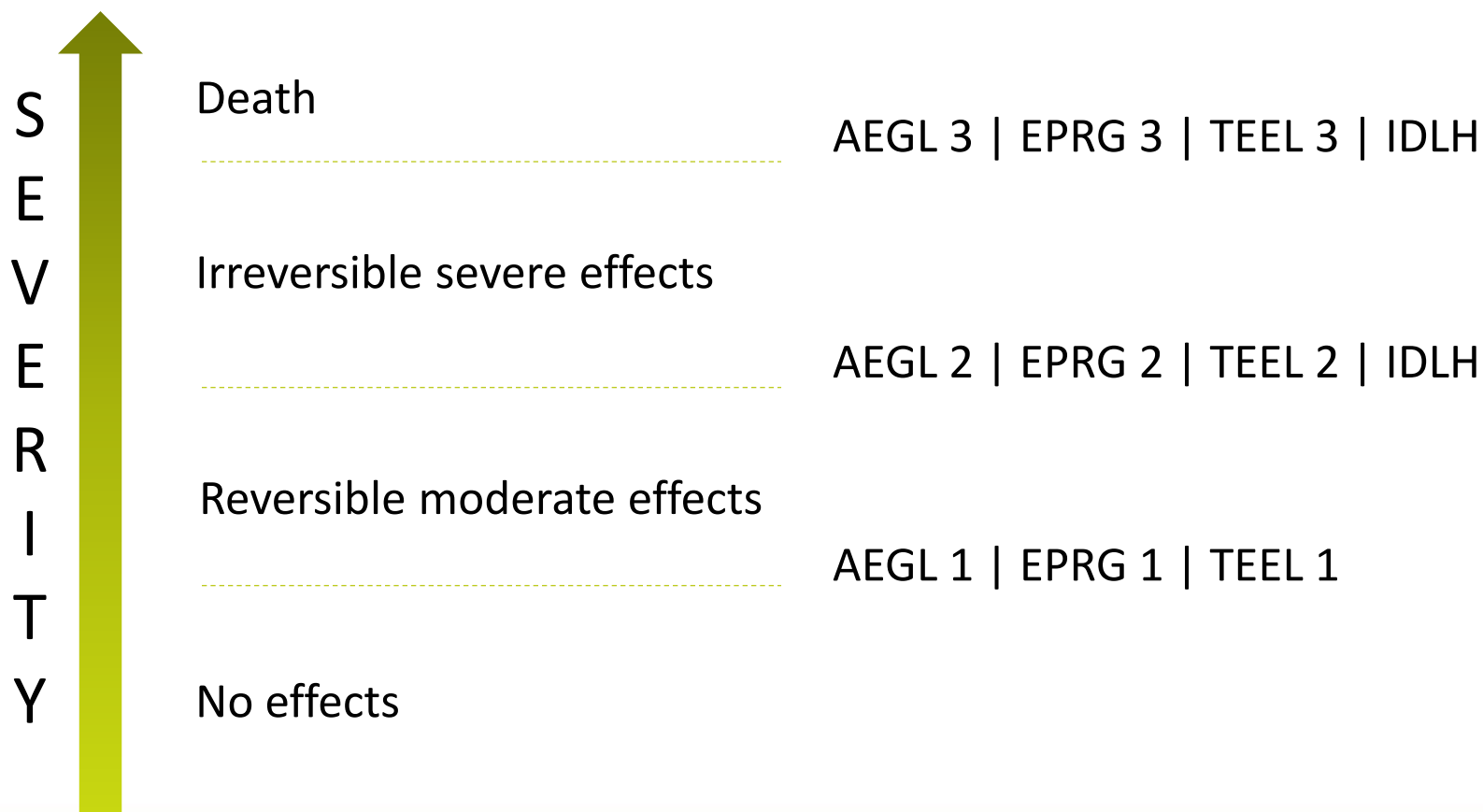


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To summarize



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To summarize

| Value | Target population | Publishing agency | Time of exposure | Values published |
|-------|---|---|----------------------|------------------|
| IDLH | Workers | National Institute for Occupational Safety and Health (NIOSH) | 30' | 390 |
| AEGL | General population, including sensitive individuals | National Academy of Sciences | 10', 30', 1h, 4h, 8h | 70 |
| EPRG | General population | American Industrial Hygiene Association (AIHA) | 1h | 145 |
| TEEL | General population, including sensitive individuals | US Department of Energy | 1h | > 3,000 |

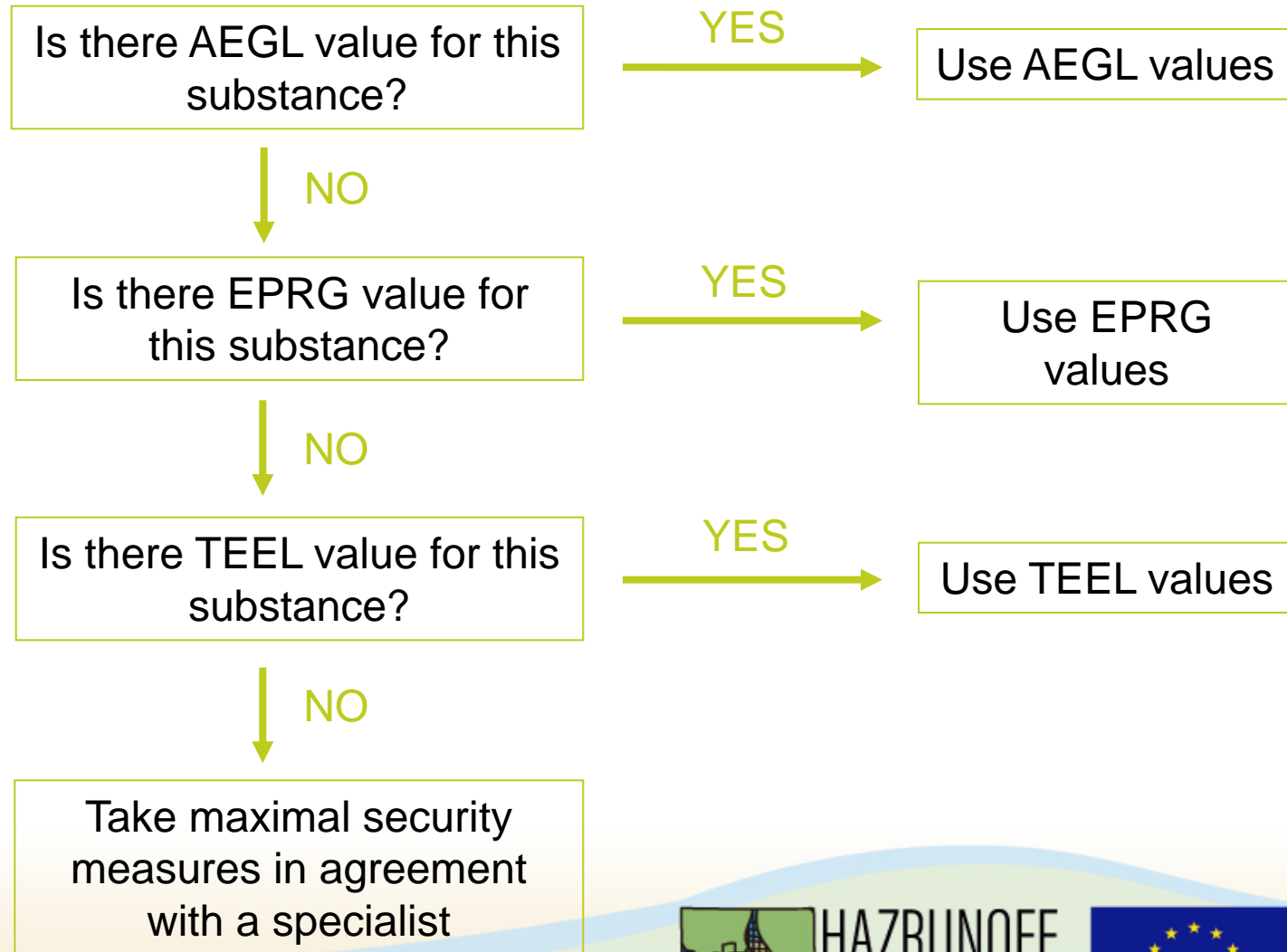


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Choosing the right value in case of an incident



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Examples – 1 h exposure

| Chemicals | AEGL 3 | EPRG 3 | TEEL 3 |
|------------------|-----------|---------|------------|
| Ammonia | 1,100 ppm | 750 ppm | n/a |
| Carbone monoxide | 330 ppm | 500 ppm | n/a |
| Chlorine | 20 ppm | 20 ppm | n/a |
| Hydrogen bromide | 120 ppm | n/a | n/a |
| Nitrous oxide | n/a | n/a | 20,000 ppm |

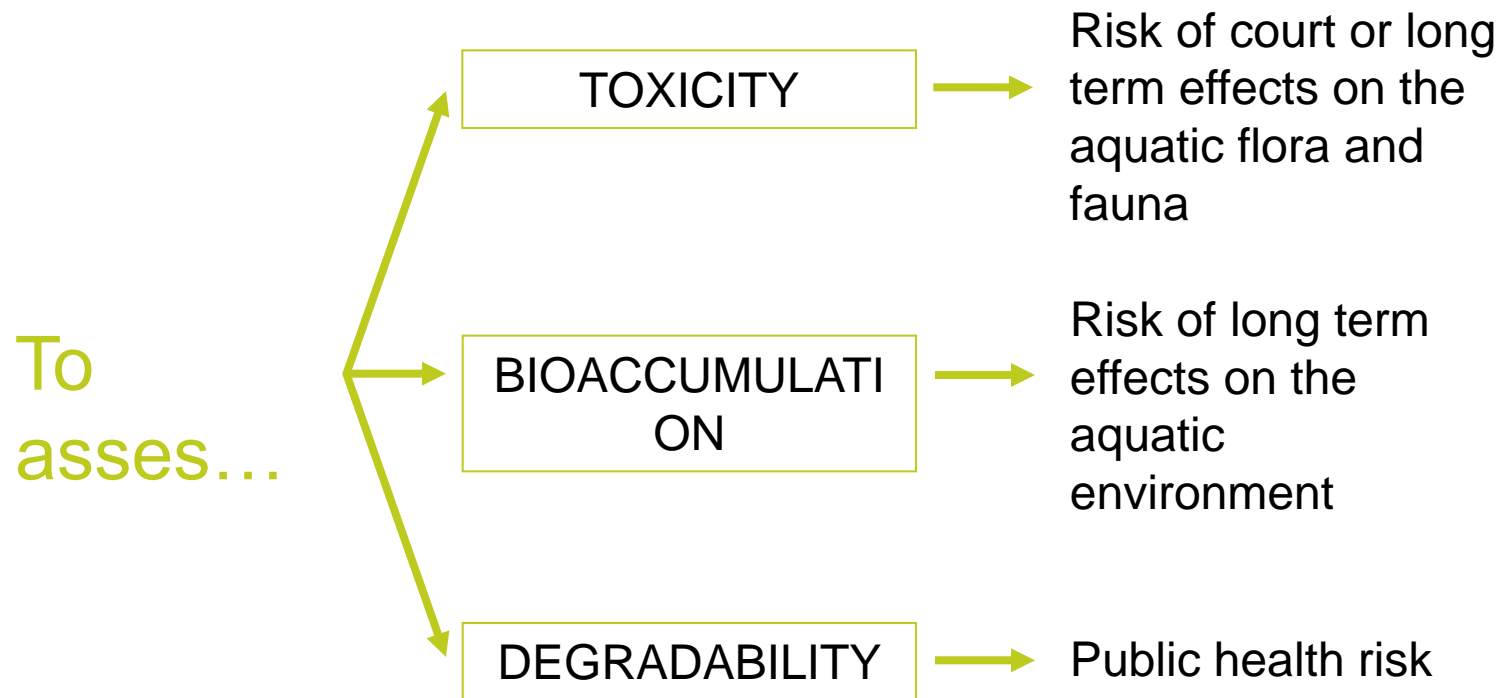


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Why do we need environmental limits?



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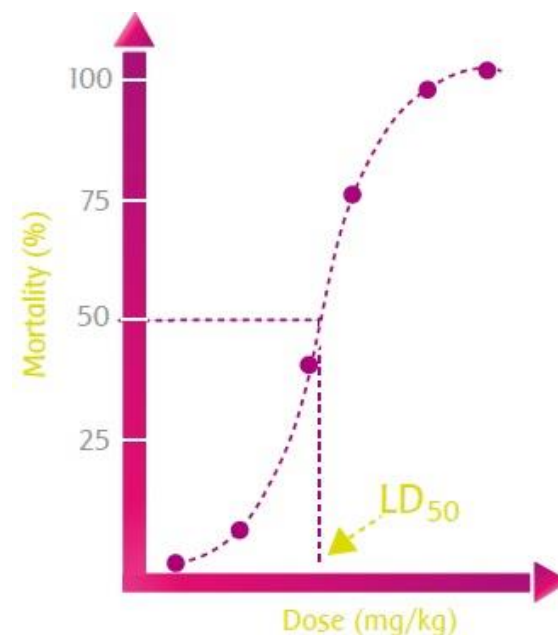
LD₅₀ and LC₅₀

LD₅₀:

The dose of a substance that will kill 50% of a given population in specific experimental conditions. It is expressed in milligrams of a substance per kilogram of animal body mass (mg/kg).

LC₅₀:

In the case of a gas or liquid, the median lethal concentration (LC₅₀) is calculated and expressed in milligrams per litre (mg/L) or parts per million (ppm).



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| | |
|-------------------------|-----------------|
| DDT (rainbow trout) | 3 to 6 µg/L |
| Lindane (rainbow trout) | 20 to 36 µg/L |
| TEPP (rainbow trout) | 500 to 980 µg/L |

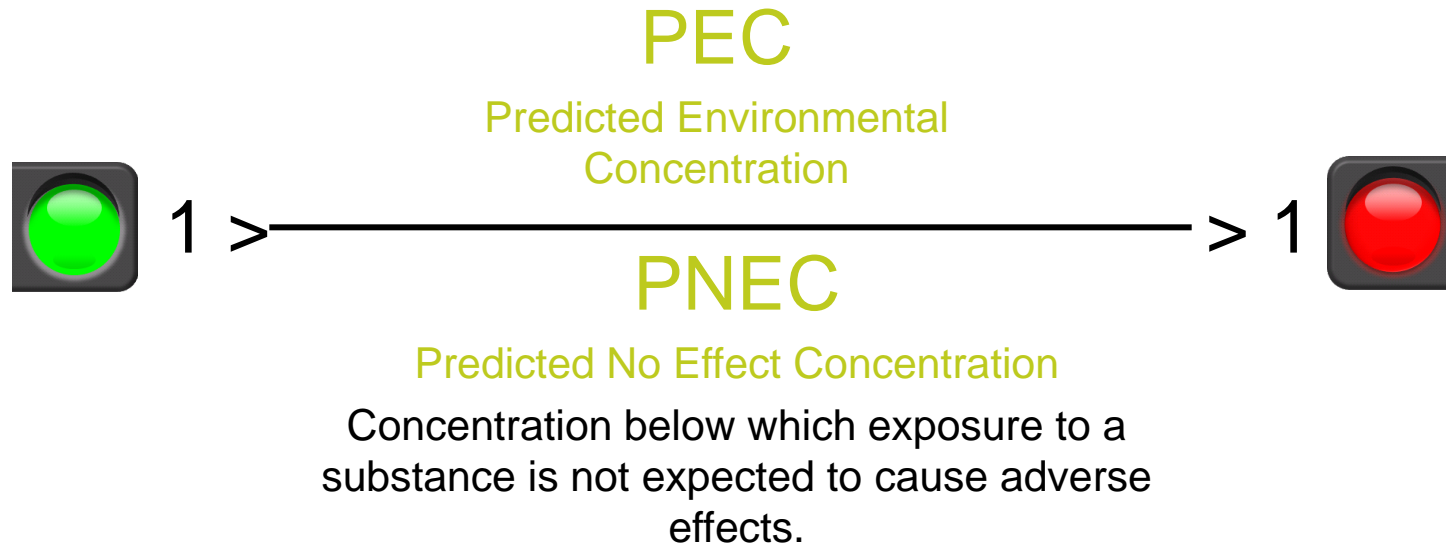


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PEC/PNEC



| | |
|------------|----------|
| Chromium | 0.6 µg/L |
| Benzene | 8 µg/L |
| Chloroform | 146 µg/L |
| Methanol | 154 mg/L |



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BCF (Bioconcentration factor)

[substance] in organism

[substance] in water

$BCF > 4,000$

Very
bioaccumulable

$4,000 > BCF > 500$

Bioaccumulable

$BCF < 500$

Little
bioaccumulable

| | |
|----------------|---------------------|
| Vinyl chloride | 10 to 40 L/kg |
| Xylene | 72 to 106 L/kg |
| Mercury | 5,000 to 9,000 L/kg |



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Kow and Log Kow

$$\text{Kow} = \frac{\text{[substance] in octanol}}{\text{[substance] in water}}$$

Kow defines the ability for a substance to be lipid soluble, so its ability to bioconcentrate in the tissues.

Non accumulable  $1 < \text{Log Kow} < 7$  Highly accumulable

| | |
|----------------|------|
| Vinyl chloride | 1.58 |
| Chloroform | 2.13 |
| DDT | 6.4 |



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Half life

Time in the course of which a fraction representing 50 % of the initial quantity is degraded.

Abiotic degradation:

Hydrolyse

Photodegradation

| | |
|------------------|-----------|
| Styrene (air) | 7 to 16 h |
|------------------|-----------|

Biodegradation:

Water

Sediment

| | |
|--------------------------|-------------|
| Glyphosate (seawater) | 47 to 315 d |
|--------------------------|-------------|



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Example of a biomonitoring:

Assessing the environmental impact of the *COSTA CONCORDIA* wreck through an integrated, multidisciplinary weight of evidence approach



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Example of a biomonitoring



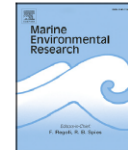
Marine Environmental Research 96 (2014) 92–104



Contents lists available at ScienceDirect

Marine Environmental Research

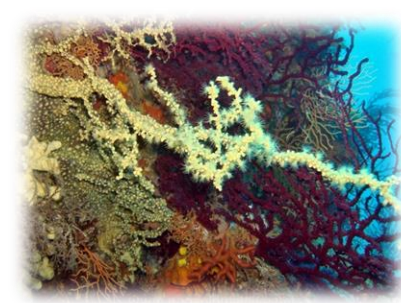
journal homepage: www.elsevier.com/locate/marenvrev



A multidisciplinary weight of evidence approach for environmental risk assessment at the Costa Concordia wreck: Integrative indices from Mussel Watch



Francesco Regoli^{a,*}, David Pellegrini^b, Anna Maria Cicero^c, Marco Nigro^d,
Maura Benedetti^a, Stefania Gorbi^a, Daniele Fattorini^a, Giuseppe D'Errico^a,
Marta Di Carlo^a, Alessandro Nardi^a, Andrea Gaion^b, Alice Scuderi^b, Silvia Giuliani^b,
Giulia Romanelli^c, Daniela Berto^e, Benedetta Trabucco^c, Patrizia Guidi^d,
Margherita Bernardeschi^d, Vittoria Scarcelli^d, Giada Frenzilli^d



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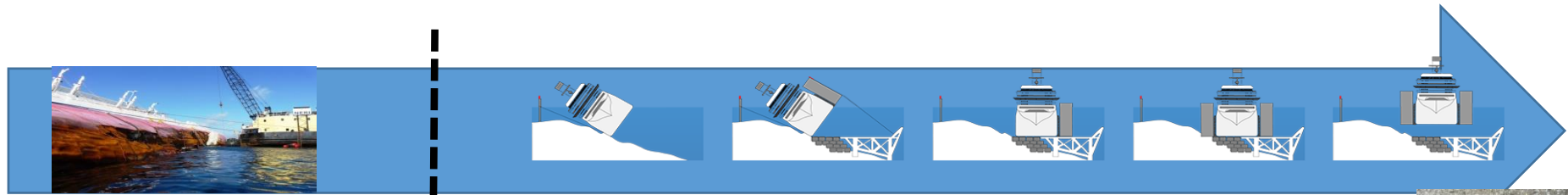


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Treatment of the Costa Concordia wreck



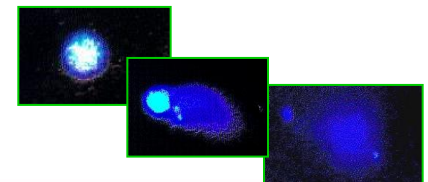
EMERGENCY PHASE

PARBUCKLING PROJECT



Implementation of an environmental biomonitoring programme

| Sampling dates | I Campaign Jan 2012 | II Campaign Mar 2012 | III Campaign Apr 2012 | IV Campaign May 2012 | V Campaign Jun 2012 | VI Campaign Jul 2012 | VII Campaign Oct 2012 | VIII Campaign Dec 2012 | IX Campaign Jan 2013 | X Campaign Apr 2013 |
|------------------------------|--|-------------------------|--------------------------|-------------------------|------------------------|---|--------------------------|---------------------------|-------------------------|------------------------|
| To look for which pollutants | Bioavailability <ul style="list-style-type: none"> - Trace metals - Polycyclic Aromatic Hydrocarbons PAHs - Volatile hydrocarbons C6-C10 - Aliphatic hydrocarbons C10-C40 | | | | | <ul style="list-style-type: none"> - Halogenated pesticides - Polychlorinated biphenyls PCBs - Organotin compounds - Flame retardants (PBDE) - Anionic surfactants | | | | |
| By biomarkers measurements | Detoxification-Exposure biomarkers <ul style="list-style-type: none"> - Metallothioneins - Peroxisomal proliferation - Cytochrome P450 and bile metabolites - Acetylcholinesterase Oxidative stress <ul style="list-style-type: none"> - Antioxidants and antioxidant enzymes - Total antioxidant capacity | | | | | Cellular damage <ul style="list-style-type: none"> - Lysosomal stability - Lipofuscin and neutral lipids - Lipid peroxidation Genotoxic effects <ul style="list-style-type: none"> - DNA integrity - Micronuclei and nuclear alterations | | | | |

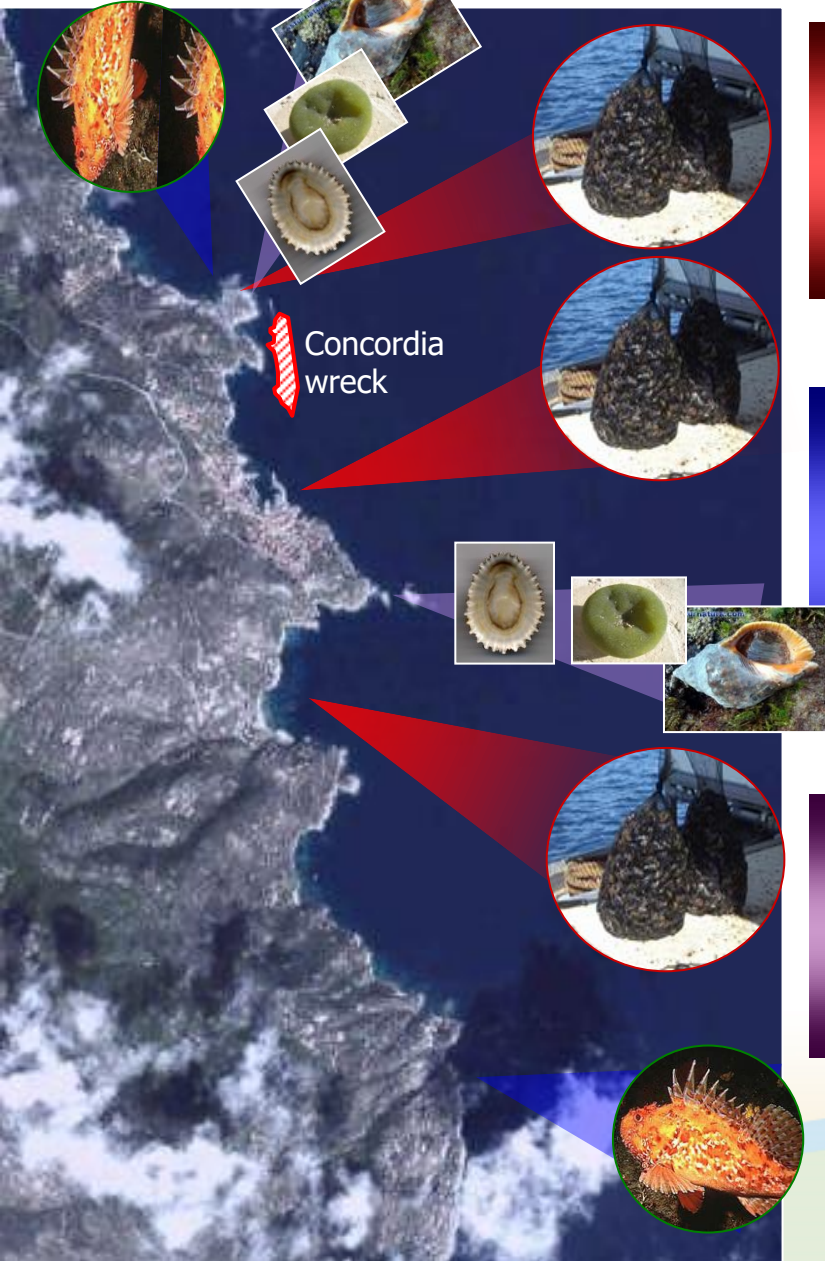


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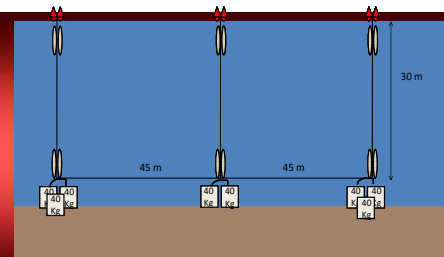
Implementation of the environmental monitoring



Concordia wreck

Active Mussel Watch

Short term chemical spill and impact
3 sites, 2 depths



Bioavailability and long term effects in native fish Species of different trophic levels

- Scorpion fish (*Scorpaena* sp.)
- Red mullet (*Mullus barbatus*)
- Forkbeard (*Phycis blennoides*)
- Stargaze (*Uranoscopus scaber*)



Rocky shore invertebrates, algae:
different exposure route and chemical persistence
on rocks.

- *Thais haemastoma*
- *Patella* sp.
- *Codium bursa*



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How to expose the results

Need to express the results in an understandable way... **and not –only- in a purely scientific way!**

Methodology followed

- Calculation for each biomarker of the variation compared to Threshold, corrected for statistical significance and importance of biomarker (score)
- Assignment of each biomarker response to 1 of 5 classes of effect
- Calculation and Classification of cumulative HQ in a level of hazard according to % distribution of biomarkers in the 5 classes

Tab_biomarker

LOE3 biomarkers

ID:

281

Latitude:

Longitude:

Area_code:

Isola del Giglio

Site_code:

Concordia

Reference_Area_code:

Isola del Giglio

Reference_Site_code:

Concordia

Sampling_date:

01/04/2012

Sampling_code:

conc_pes_apr_12

Core_code:

Core_level:

Experimental condition:

Wild organisms

Exposure_time:

Species:

Scorpaena_spp

Sample_code:

Scorpaena_scrofa_nave_apr_12

Reference_Sample_code:

Scorpaena_scrofa_bianco_apr_12

Note:

Scorpaena_scrofa

RESULTS

| | Weighted mean | n° biomarker |
|---------|---------------|--------------|
| Class A | 0 | 12 |
| Class B | 1,288312 | 2 |
| Class C | 1,477815 | 2 |
| Class D | 0 | 0 |
| Class E | 0 | 0 |

Cumulative HQ for biomarkers

Level of hazard for biomarkers

HQ

1,477815

SLIGHT

Absent

Slight

Moderate

Major

Severe

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Biomonitoring results

- Bioavailability data exclude serious contamination events from the wreck or a consistent increase of environmental pollutants
- Nonetheless, **moderate or episodic spills with reversible effects have been detected**, differing between the emergency phase and the operations for removal
- The more evident bioaccumulation trend in *T. haemastoma* suggests different exposure dynamics on rocky shores due to a re-washing effect
- Consistently with bioaccumulation, biomarkers did not reveal major effects on the health condition of both transplanted or native organisms, still allowing a very sensitive detection of early biological disturbance
- The Weight of Evidence approach and the presented model were confirmed useful to summarize large datasets of different typologies of data, for characterizing environmental quality and risk assessment in a comprehensive process of “site-oriented” management decisions

<http://www.disva.univpm.it/content/ecotoxicology-and-environmental-chemistry?language=en>



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Key points

Substance hazard

Ecotoxicology data

Response of relevant biomarkers

Impact at the population and/or community levels

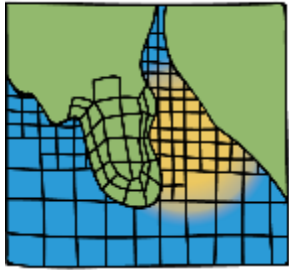
Need to mix different tools



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