Valutazione del rischio chimico

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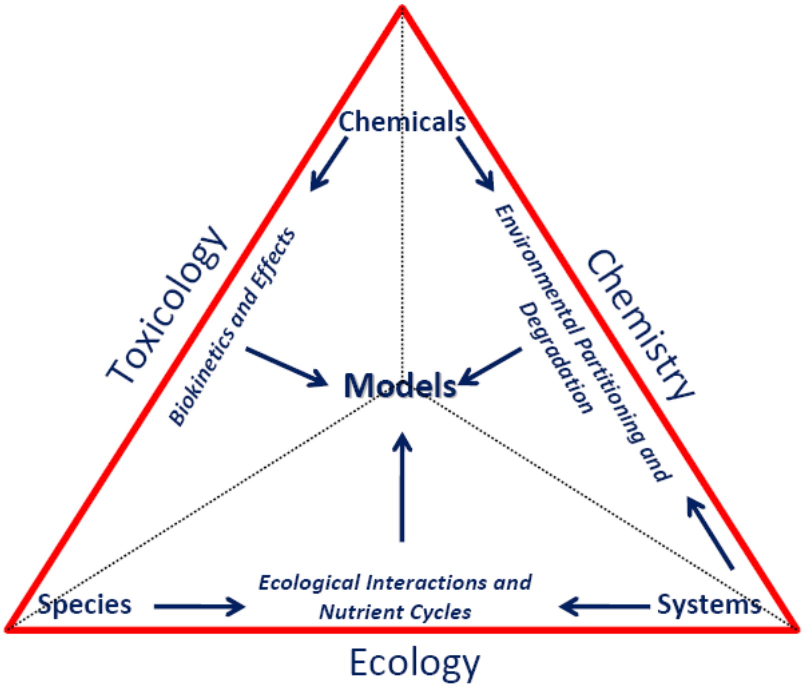
Ecotossicologia: scienza delle tre S



Redrawn from Figure 7.1 of van Leeuwen and Vermeire (2007)

Table 6.1. "Disciplines" of ecotoxicology and some of their research topics

Chemistry	Toxicology	Ecology	Mathematics
Exposure assessment	effects assessment	community structure	environmental fate models
Transport	modes of toxic action	community functions	pharmacokinetic models
Partitioning	bioaccumulation	population dynamics	LC50 and NOEC statistics
Transformation	biotransformation	nutrient/energy cycling	species-species extrapolation
SARs/QSARs	extrapolation	various interactions	population and ecosystem models

Tossicologia acquatica

Gli studi sugli organismi acquatici sono di prima generazione, i più diffusi, i più consolidati
Misure basate su effetti a breve termine, o Saggi acuti:
da pochi minuti (batteri luminescenti) a 24 o 96 h (pesci, crostacei).

Valutazioni: effetti prodotti da immissioni, più o meno accidentali, di sostanze diverse, di pesticidi, di reflui industriali o domestici

Specie animali: pesci, invertebrati
Specie vegetali: microalghe

Scopo: rilevare la concentrazione o la dose di una sostanza o di una miscela, di un agente fisico (torbidità, livello termico, radiazioni ionizzanti) che hanno effetto avverso misurabile per gli organismi considerati

PREGI

Il saggio tossicologico diviene estremamente utile ai fini della valutazione delle interazioni tra le componenti tossiche e le caratteristiche naturali del corpo idrico ricevente.

LIMITAZIONI

L'approccio tradizionale basato sull'utilizzazione di *una singola specie* può essere riduttivo rispetto alla complessità degli ecosistemi

L'utilizzazione di un *numero maggiore di specie lascia comunque irrisolti i problemi di incertezza* rispetto alla capacità di tolleranza delle innumerevoli specie (micro e macrospiche) di un ecosistema acquatico

I saggi a *breve termine*, prevalentemente utilizzati, non permettono di prevedere quali siano invece gli effetti derivanti da esposizione a lungo termine

Individuazione *a priori* dei **percorsi critici** degli inquinanti (quelli in cui si prevedono le contaminazioni maggiori) e dei **gruppi critici** (specie o insiemi di individui più esposti alla contaminazione).

Si controllano gruppi critici e/o i percorsi critici, e si assume che se per essi sono verificate condizioni accettabili, allora anche altre specie, individui, siti si trovino in condizioni di sicurezza.

SEDIMENTI

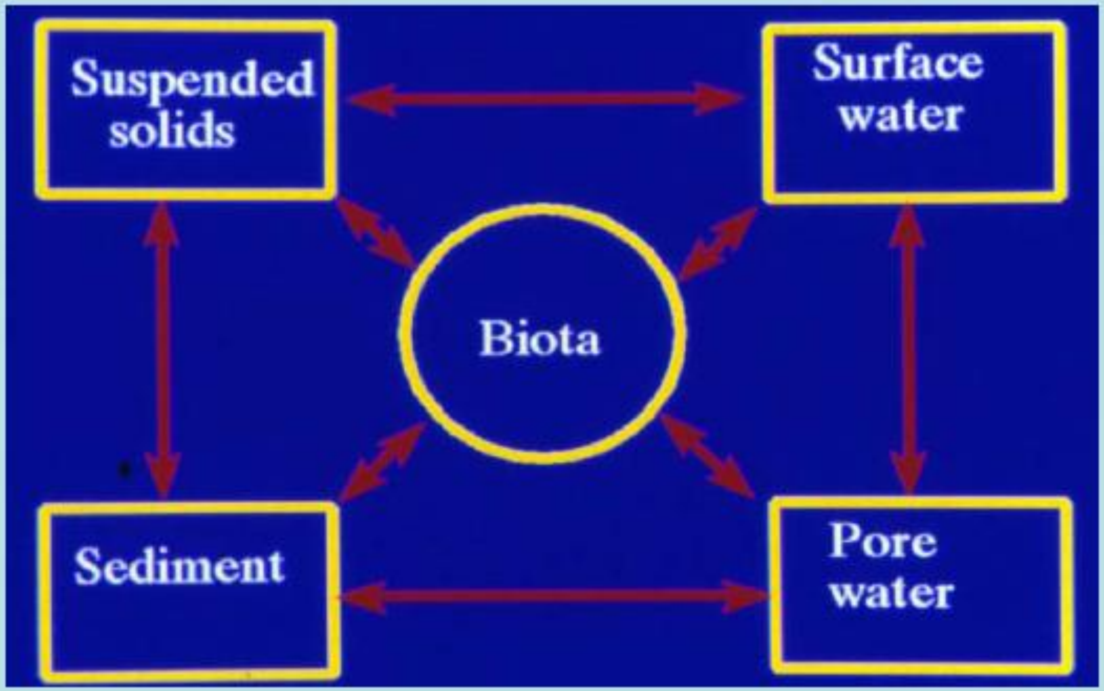


Fig. 7.26. Compartments and their interrelationships

EQUILIBRIUM-PARTITIONING

(Van der Kooy et al., 1990)

CONCENTRATIONS IN WATER AND SOLIDS ARE RELATED THROUGH A PARTITION COEFFICIENT:

$$Ksw = \frac{Cs}{Cw}$$

WHERE:

Ksw = SOLIDS-WATER PARTITION COEFFICIENT (L/KG)

CS = CONCENTRATION IN THE SOLID PHASE (MG/KG)

CW = CONCENTRATION IN THE WATER PHASE (MG/L)

Sediment Quality Guidelines developed for the National Status and Trends Program

Because guidelines were needed that were based on measures of biological effects associated with toxicants, data were compiled that included both chemical measures and biological effects.

SQGs were derived initially using a database compiled from studies performed in both saltwater and freshwater and published in NOAA Technical Memorandum NOS OMA 52 (Long and Morgan 1990). A larger database compiled from many
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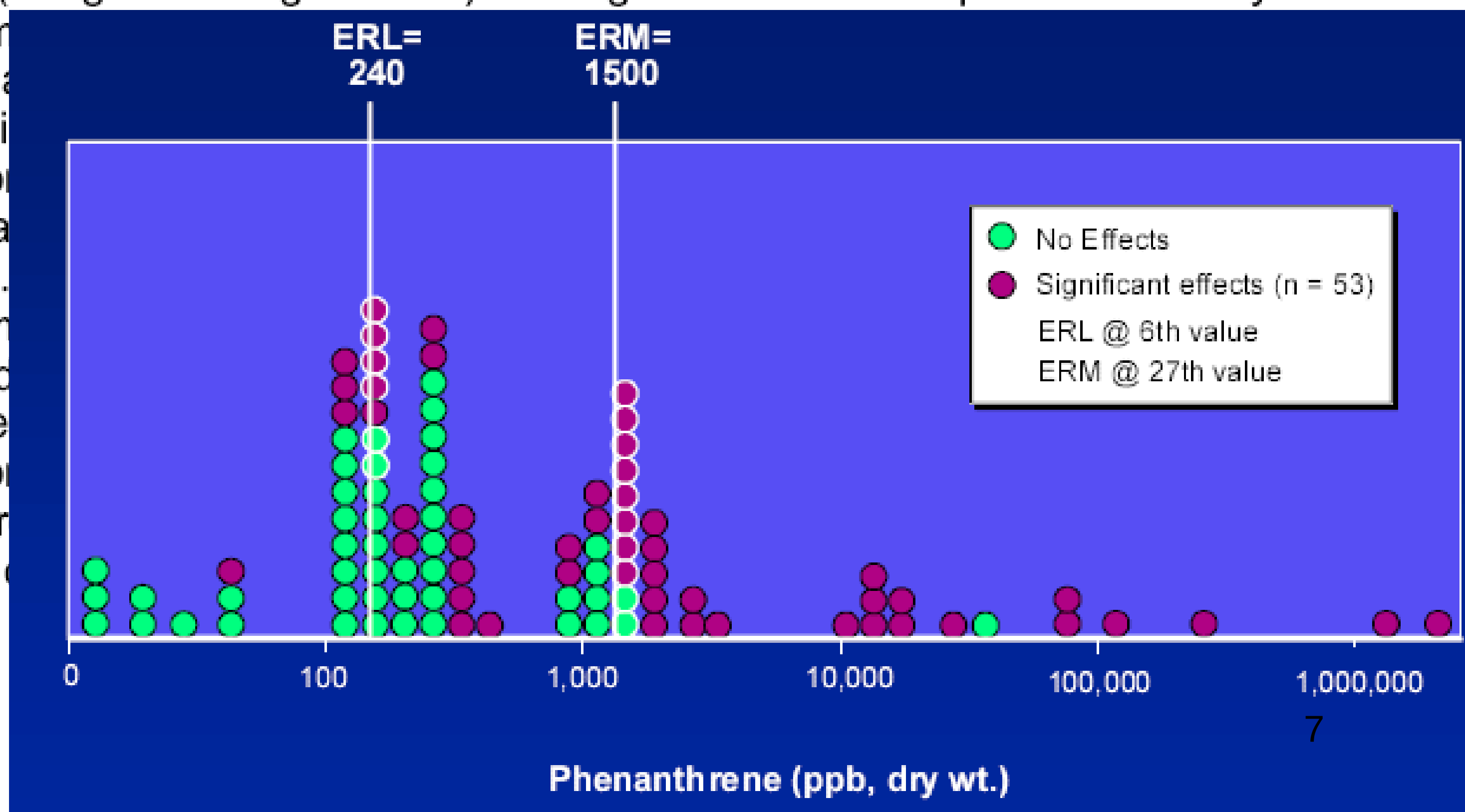

Table 1. ERL and ERM guideline values for trace metals (ppm, dry wt.) and percent incidence of biological effects in concentration ranges defined by the two values (from Long et al., 1995). ERL= Effects Range-Low; ERM= Effects Range-Median.

	Guidelines		Percent incidence of effects*		
Chemical	ERL	ERM	<ERL	ERL - ERM	>ERM
Arsenic	8.2	70	5.0	11.1	63.0
Cadmium	1.2	9.6	6.6	36.6	65.7
Chromium	81	370	2.9	21.1	95.0
Copper	34	270	9.4	29.1	83.7
Lead	46.7	218	8.0	35.8	90.2
Mercury	0.15	0.71	8.3	23.5	42.3
Nickel	20.9	51.6	1.9	16.7	16.9
Silver	1.0	3.7	2.6	32.3	92.8
Zinc	150	410	6.1	47.0	69.8

*Number of data entries within each concentration range in which biological effects were observed divided by the total number of entries within each range.

Table 2. ERL and ERM guideline values for organic compounds (ppb, dry wt.) and percent incidence of biological effects in concentration ranges defined by the two values (from Long et al. 1995). ERL= Effects Range-Low; ERM= Effects Range-Median.

	Guidelines		Percent incidence of effects*		
Chemical	ERL	ERM	<ERL	ERL--ERM	>ERM
Acenaphthene	16	500	20.0	32.4	84.2
Acenaphthylene	44	640	14.3	17.9	100
Anthracene	85.3	1100	25.0	44.2	85.2
Fluorene	19	540	27.3	36.5	86.7
2-methyl naphthalene	70	670	12.5	73.3	100
Naphthalene	160	2100	16.0	41.0	88.9
Phenanthrene	240	1500	18.5	46.2	90.3
Sum LPAH	552	3160	13.0	48.1	100
Benz(a)anthracene	261	1600	21.1	43.8	92.6
Benzo(a)pyrene	430	1600	10.3	63.0	80.0
Chrysene	384	2800	19.0	45.0	88.5
Dibenzo (a,h) anthracene	63.4	260	11.5	54.5	66.7
Fluoranthene	600	5100	20.6	63.6	92.3
Pyrene	665	2600	17.2	53.1	87.5
Sum HPAH	1700	9600	10.5	40.0	81.2
Sum of total PAH	4022	44792	14.3	36.1	85.0
p,p'-DDE	2.2	27	5.0	50.0	50.0
Sum total DDTs	1.58	46.1	20.0	75.0	53.6
Total PCBs	22.7	180	18.5	40.8	51.0

*Number of data entries within each concentration range in which biological effects were observed divided by the total number of entries within each range.

Preliminar Results From a Sediment Quality Triad Study in the Gulf of Trieste:

the Choice of the Reference Site.

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Title anticipated in the Book of Abstracts:
"Sediment Quality Triads and the Integration of Information from Analytical Chemistry with Ecological Community Structure and Toxicological Data in Risk Assessment of Coastal Sites."

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Environmental quality criteria

Aiming at the classification of ecosystems on the base of their environmental degradation, *environmental quality criteria* (numerical values) are required in order to determine if a zone is degraded or not.

Questions arise when the environmental quality criteria is based only on the assessment of chemical contamination of a certain environmental compartment since *chemical contamination does not necessarily imply effects on biological communities*. Moreover effects on biological communities are related to several factors, conditioning also the concentrations of contaminants, as – in aquatic systems – hydrodynamics, grain size of sediments, species being considered, etcetera.

Sediments

Within aquatic ecosystems, sediments achieve importance in consideration of:

- Accumulation of contaminants (low solubility – affinity for particulate matter
- High residence time of c. (difficult biodegradation in reducing medium) → benthic organisms exposed to high levels of c.
- Sediment bound contaminants can be released to water if environmental conditions do vary.

Environmental agencies - as U.S.E.P.A. - thus consider *sediments as key environmental components within aquatic compartments.*

Criteria classically determined for environmental quality characterisation derive from approaches listed in Table 1, where examples and main limitations of each are reported.

Table1

APPROACH	*EXAMPLE OF MEASUREMENTS*	*LIMITATIONS*
Sediment chemical analyses	- Individual contaminants - Complementary analyses (TOC, surface of grains etc.)	- Assumes that all chemical contaminants are measured - Contamination do not inform about biological effects
Organism tissue chemical analyses	- Individual contaminants - Complementary analyses (biometrical etc.)	- *Idem* as above - Organisms mobility
Sediment toxicity tests	- Survival - Sublethal effects (malformation, burial)	- Conditions different from reality; - Assumes that considered tests cover all responses - Toxicity is not linked causally to specific toxic agent
Histopathological alterations	- Individual pathological conditions - Complementary analyses (biometrical etc.)	- Organisms mobility - Disease is not linked causally to specific chemical agent
Structure of the Benthic community	- Taxa (Mollusca, Polichaeta etc.) - Biomass; indices of biodiversity	- Difficult to discriminate between natural and anthropogenic effects

Each single approach presents pros and cons; consequently two or more of the cited type of measurements can be applied on samples acquired simultaneously thus allowing *an integrated assessment*.

The case study

The growing degree of connection of urban and industrial sites of the Plain of the Isonzo River to the local sewage treatment plants and the high environmental pressure on the coast line of the Gulf of Trieste have brought to *plan the building of a new off-shore diffusor* that will be completed before the end of 2002.

Other diffusors within the same Gulf were demonstrated to bring metals to offshore sediments, thus extending the radius of impact of human activities, beside lowering the environmental strain on the coastline [].

An *integrated environmental assessment* has been performed before the building and exersice of the offshore dispersion device *at four sites located nearby* it -locations are ISO1, ISO2, ISO3 and ISO4 in Figure 1 - so to provide a reference for a future evaluation the possible impact of treated waters on benthic life. *Measurements describing chemical contamination of sediments, ecotoxicity tests with sediment elutriates, and quali-quantitative assessment of macrobenthic population have been produced.*

	Long.	Lat.
ISO1	13°35'.43	45°42'.08
ISO2	13°35'.17	45°41'.86
ISO3	13°35'.91	45°42'.13
ISO4	13°35'.33	45°42'.73

	Depth (m)	Sand %	Silt %	Clay %
ISO1	13.7	0.00	33.47	63.53
ISO2	13.7	0.00	33.16	66.84
ISO3	14.6	0.00	37.05	62.95
ISO4	11.5	0.00	42.82	57.18

Experimental methods:

Samples for chemical and toxicological analyses have been collected by a Kc HAPS bottom corer with a sample area of 127 cm^2; for the analysis of benthos three samples have been collected with a 0.1 m^2 van Veen grab.

Chemical analyses: metals (Cd, Ni, Pb, Ag, Cu, Cr, Fe, Zn, As and Hg) have been released from sediments and analysed according to I.R.S.A. methodologies []. The spectrometer was a PE-5100PC.

PAHs (Phenantrene, Fluoranthene, Pyrene, Benzo(a)anthracene, Crysene, Benzo(b)fluoranthene, Benzo(a)pyrene), PCBs, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT have been extracted again according to I.R.S.A. methods []; PCBs have been quantified as PCB1254 mixture. The separation were conducted by gas chromatography, with ECD for chlorinated compounds and MS for PAHs. PE-AutoSystem XL and HP-6980/5973 instruments were used.

Toxicological analyses on sediment elutriates considered here are the Microtox assay® [] and the assay on the alga *Dunaliella tertiolecta* [].

In situ alteration of the benthic community has been assessed by the *analysis of macrobenthos.* Macrobenthic organisms (Mollusca, Polychaeta, Crustacea, Echinodermata) have been determined to species level; furthermore abundance values of specimens were computed. From these data diversity indices (Shannon, Pielou) have been calculated.

Chemistry, Toxicity and Infauna Data from the four different sites can be combined into *the Sediment Quality Triad* (SQT) [] in order to determine the degree of degradation at each site. The normalization of data from the sampling sites towards those of one of them that is considered as an unpolluted reference makes the comparison relatively easy. For each site and for each parameter determined, the datum is converted into a *Ratio To Reference* (RTR) value:

$$(RTR_i)_k = (v_i)_k / (v_i)_0$$ where:

$(RTR_i)_k$ is the RTR for parameter i-me at site k-me;

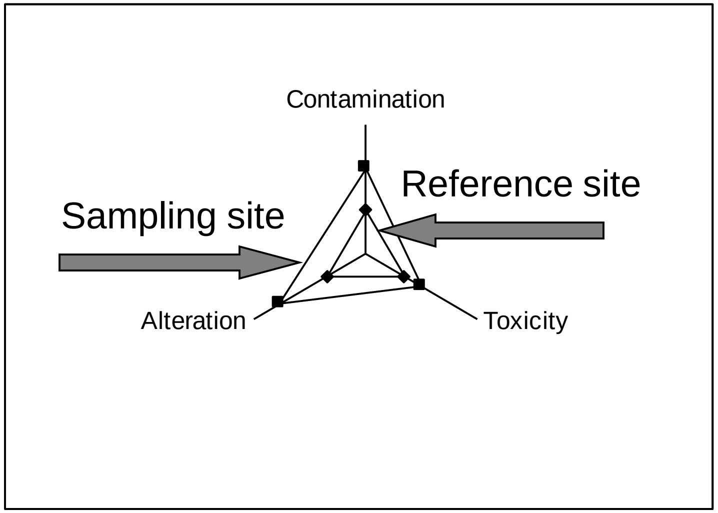
$(v_i)_k$ is the datum determined for parameter i-me at site k-me;

$(v_i)_0$ is the datum determined for parameter i-me at site chosen as reference.

This is straightforward for chemical parameters, while toxicological and infaunal parameters have been transformed so to show increase with biological damage. For instance, in a Microtox® test the result (endpoint) is expressed as EC20, the percentage of interstitial water sample causing a 20% inhibition of bioluminescence of the population of *Vibrio Fisheri;* this means that EC20 is low when sediment is highly polluted; the inverse ($EC20^{-1}$) is thus considered.

$(RTR_i)_k$ for all i parameters describing chemical contamination are averaged, thus providing a single *Index of Contamination for each site, IC ;* the same is done for parameters describing sediment toxicity and *in situ* alteration; The result is a *Index of Toxicity (IT) and a Index of Alteration (IA) for each site*.

The three indices for each sampling site can be displayed in graphical form as three segments (for Contamination, Toxicity and Alteration) departing from a central point, where the lenghts of each segment equals the averaged values of the RTR for the three group of determined parameters.



Two triangles are identified; the inner one represents the reference site, the outer is one of the site for whom the environmental quality must be assessed. The difference between the areas of the outer and inner triangles can be retained as a synthetic ***index of degradation*** with respect of the reference site []. The difference between the sums of the three indices IC, IT and IA. for the site under investigation and the reference is a measure of degradation as well.

Del Valls et al. [] proposed a modified normalization procedure, where:

$$(RTM_i)_k = (RTR_i)_k / RTRmax_i$$

$(RTM_i)_k$ is the new normalized value for parameter i-me at site k-me;

$(RTR_i)_k$ is the RTR for parameter i-me at site k-me;

$RTRmax_i$ is the maximum value of RTR for parameter i-me;

The new indices of Contamination, Toxicity and Alteration for site k are computed as:

$NIC_k=(\Sigma RTM_{ic})_k / (\Sigma RTM_{i\,c})_0$; ic = index running between chemical parameters;

$NIT_k=(\Sigma RTM_{it})_k / (\Sigma RTM_{i\,t})_0$; it = index running between toxicological parameters;

$NIA_k=(\Sigma RTM_{ia})_k / (\Sigma RTM_{i\,a})_0$; ia = index running between alteration parameters

It is clear how results depend on the choice of the reference site, but no formal procedure has been proposed to select it, at the best of our knowledge.

The problem is not trivial, since in practical cases it is frequent to choose the reference site between stations which are not “completely unpolluted”; the quest for a “truly unpolluted” reference could lead to select a station being too heterogeneous from others.

A formal procedure for selecting the reference site is as follows:

1) for each possible reference site i

compute IC, IT, IA (or NIC, NIT, NIA) and index of degradation P_{ij} (based on areas of triangle or on sums of indices) for each sampling site j

2) the selected reference site $\underline{i}$ is the one for which

a) $P_{\underline{ii}} = \min P_{ij}$;

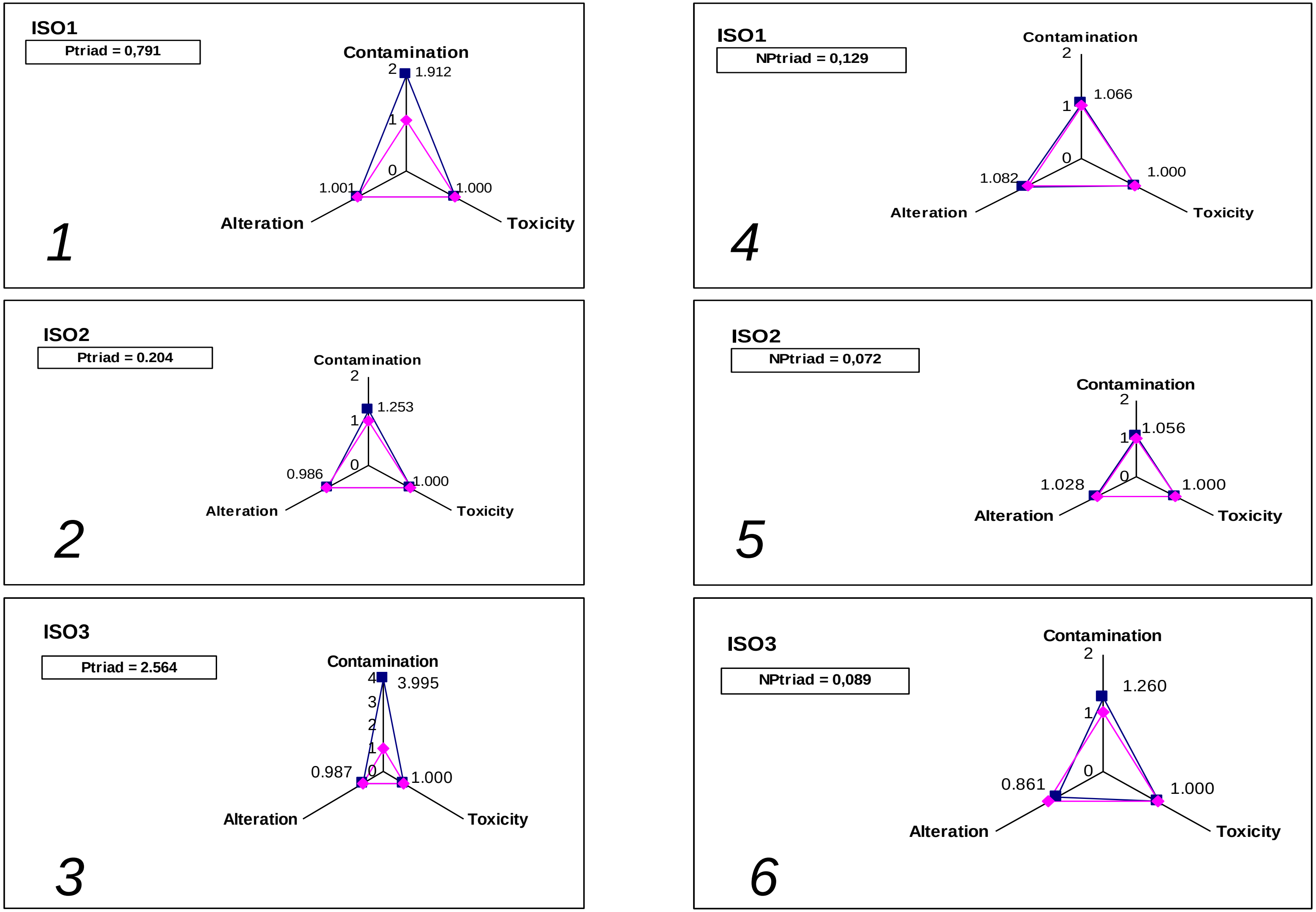
b) $P_{\underline{i}j} \geq 0$.

The results of the procedure described above for our data, using RTR, the areas for defining the index of degradation, are as follows:

Rif.	**ISO1**				**ISO2**				**ISO3**				**ISO4**			
	ISO1	**ISO2**	**ISO3**	**ISO4**	**ISO1**	**ISO2**	**ISO3**	**ISO4**	**ISO1**	**ISO2**	**ISO3**	**ISO4**	**ISO1**	**ISO2**	**ISO3**	**ISO4**
IC	1.000	0.989	1.760	0.908	1.193	1.000	2.423	0.903	1.193	1.000	2.423	0.903	1.912	1.253	3.995	1.000
IT	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
IA	1.000	0.992	0.791	0.939	1.016	1.000	1.001	1.015	1.016	1.000	1.001	1.015	1.001	0.986	0.987	1.000
Ptriad	**0.000**	**-0.017**	**0.407**	**-0.131**	**0.181**	**0.000**	**1.233**	**-0.073**	**0.181**	**0.000**	**1.233**	**-0.073**	***0.791***	***0.204***	***2.564***	***0.000***

Underlined numbers stand for condition (a), Italics stand for condition (b); from the table above, *ISO4 is selected as reference site*.

Sediment Quality Triad Plots



Plots 1, 2, 3 report results derived after RTR normalization; plots 4, 5, 6 report results derived after RTM normalization; Degradation Indices (P or NP) are differences between areas of triangles defined for the sampling sites ISO1, ISO2, ISO3 , and the reference site ISO4.

Conclusions

Examining the plots it can be seen how the three sites are very similar to the reference station; some differencies can be appreciated with respect to the chemical contamination, but they seem not to be severe enough to alter in a significative way population of macrobenthos, and neither to determine a significative toxicity of sediments. This scenario will be compared with SQT analysis obtained when the wastewater diffusor will be operative.

From a methodological point of view, the SQT approach present an interesting way of synthetising complementary information, providing a rich -informative- comparison between sites of a certain area.

In order to gain more widespread acceptance of the methodology, detailed guidelines are needed so to apply SQT “on objective bases”.

Clear indications (“how to”) on the selection of contaminants to be considered, on ecotoxicological tests to be applied, and on measures of the *in situ* alteration should be set. Moreover an exaustive study on benefits of the different normalization procedures and a general criterium for the selection of the reference site are required.

In this work we have proposed a procedure for the choice of the reference station.

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- **Relative Taxa Sensitivity (RTS) of aquatic invertebrates with respect to organic and metal compounds. (39)**
- **Von der Ohe, P. & Liess, M. 2004. Environmental Toxicology and Chemistry. 23, 150-156.**
- In the field, a multitude of species can be exposed to numerous toxicants; thus, the sensitivity of individual species to particular toxicants must be known to predict effects and to analyze changes in species composition. For most species, no information about their toxicant sensitivity is available. To address this limitation, we have grouped the available information to assign sensitivities to aquatic invertebrate taxa relative to Daphnia magna. With respect to organic compounds, most taxa of the orders Anisoptera, Basommatophora, Coleoptera, Decapoda, Diptera, Ephemeroptera, Eulamellibranchiata, Heteroptera, Hirudinea, Isopoda, Oligochaeta, Prosobranchia, Trichoptera, Tricladida, and Zygoptera are less sensitive than D. magna. Some taxa of the Amphipoda, Plecoptera, and Cladocera (other than D. magna) are significantly more sensitive. For organic compounds, approximately 22% of the investigated taxa were more sensitive than D. magna. Most taxa of the orders Amphipoda, Basommatophora, Diptera, Ephemeroptera, Eulamellibranchiata, Heteroptera, Isopoda, Oligochaeta, and Tricladida are significantly less sensitive than D. magna to metal compounds. The taxa belonging to the Crustacea, with the exception of the order Isopoda, are much more sensitive. For metal compounds, approximately 30% of the investigated taxa were more sensitive than D. magna. Hence, D. magna is among the most sensitive taxa regarding both groups of toxicants. The sensitivities for several taxa are listed, and use of the relative sensitivity distribution to link toxicant effects in mesocosm studies and field investigations is discussed.