



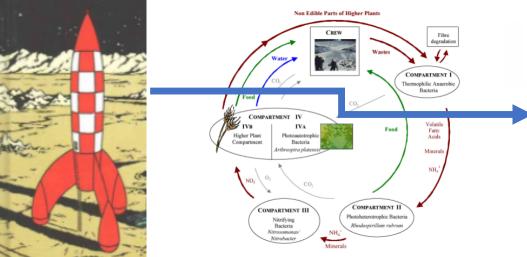
# Assessing impacts of over fifty years of launching activities on marine ecosystems

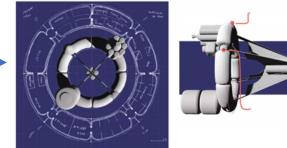
(the metal compounds case)





## The way toward a « circular future »?







**Source : didier schmitt, this conference** copyright: D. Schmitt, Red Safari, Editions Weyrich

Source : Hérgé Editions Castelman 1953





Since 2008 the Marine Strategy Framework Directive (2008/56/EC) of the European Parliament imposes to preserve and protect the marine environment

Since 2012, the space sector initiated the Clean Space initiative to investigate Life Cycle of Europe's launch vehicles and missions.

up to now ecotoxicological impacts on marine ecosystems of launching, and particularly, of launching residuals were under investigated and oversimplified.







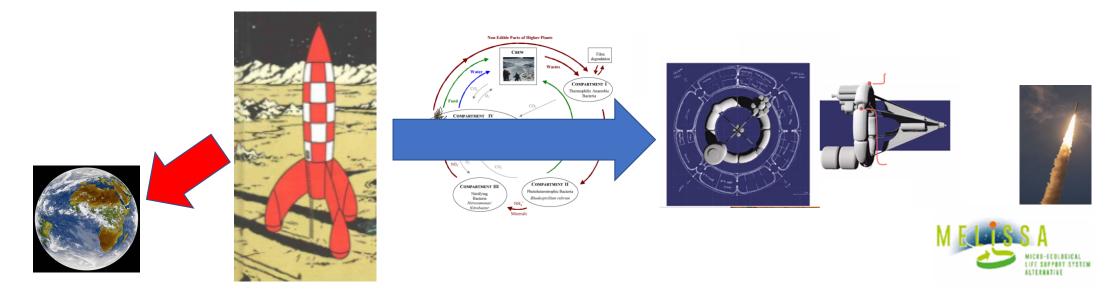






Our objectives were:

- To help ESA to face the increasing concern of its customers, stakeholders and the general Public about environmental impact of launching
- To give ESA the possibility to progressively move toward ecodesign by identifying key risk materials and suggesting design/process changes that could possibly reduce environmental impact of ESA launchers.





## Functional Ecology to Reduce Launchers Impact on Deep Sea (ESA AO 1-8623/16/NL/KML)



### ESTIMATED RELEASE to the SEA



INDUSTRY 300-500 billion kg/year (heavy metals, sludges, solvents..) ESTIMATED RELEASE to the SEA 12700 kg/sec SUN SCREEN 25000 t/year ESTIMATED RELEASE to the SEA 0,8 l/sec SHIPPING 1million t /year (gaz discharge)

ESTIMATED RELEASE to the SEA 0,76 kg/sec

LAUNCHING

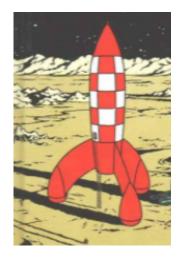
?

MELLES SA MICRO-ECOLODICAL LIFE SUPPART STATEM

Source: Comparative analysis with main reported contaminations (from UNESCO data)

# **Global IMPACT assessements**





Source : Hérgé Editions Castelman 1953





Source D. Schmitt, Red Safari Editions Weyrich 2020

From early stage



# to 21st century?



# Inventory of launcher components

- Data sources:
  - Ariane V and Vega LCA reports
  - Documentation from ESA
  - Literature review (internet search on chemistry websites, Material data sheets, Chemistry Handbook, etc.)
  - Assumptions, either on the mass and/or size of certain components, or on the type/composition of material used
- The inventory was built in several steps:
  - Determination of mass and surface for each component..
  - Decomposition in chemical elements for complex materials.
  - Compilation of physical-chemical characteristics of each chemical element and raw material from different data sources













# Estimation of total mass of launching materials returning to earth

Materials and chemical elements	Mass	oer launchers (kg/la	(kg/launch)	
Waterials and chemical elements	A5 - ECA	A5 - ES	Sum of VEGA	
Alumine	0,31	0,27	0,23	
Aluminium	20852,18	19249,43	2605,18	
Ammonium perchlorate	644,18	644,18	162,04	
Antimony	96,70	96,70	0,00	
Antimony trioxide Sb2O3	0,08	0,06	0,05	
Aramid fibre	125,40	125,40	500,50	
B/KNO3 (pyrotechnic mixture)	2,40	0,00	0,00	
Bentonite	73,35	73,35	0,00	
BeO	0,00	0,00	0,00	
Bismaleimide Triazine	0,00	0,01	0,01	

### ESTIMATED RELEASE to the SEA



INDUSTRY 300-500 billion kg/year (heavy metals, sludges, solvents..) ESTIMATED RELEASE to the SEA 12700 kg/sec

IICRO-ECOLOGICAL IFE SUPPORT SYSTEM

> SUN SCREEN 25000 t/year ESTIMATED RELEASE to the SEA 0,8 l/sec

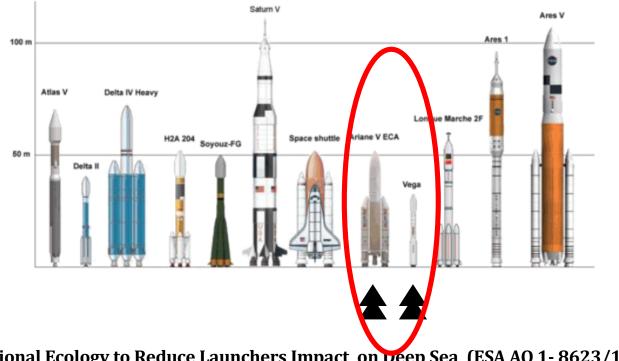
SHIPPINGLAUNCHING1million t /year(gaz discharge)ESTIMATED RELEASEESTIMATEDto the SEAESTIMATED0,76 kg/secRELEASEto the SEAto the SEA14280 t/year

0,45 kg/sec

Source: Comparative analysis with main reported contaminations (from UNESCO data)



I-Launcher composition (ARIANE and VEGA) : (Eco) toxicity of components







:

Functional Ecology to Reduce Launchers Impact on Deep Sea (ESA AO 1-8623/16/NL/KML)



#### Substances with known toxicological or ecotoxicological hazards

#### List of LD50, LC50 and EC50 of substances

materials (in Kg)					
	<1				
	1-10				
	10-70				
	70-150				
	150-500				
	500-1000				
	1000-2000				
	2000-8000				
	>19 000				

Components	Mass	Massp	Mamma	ls¤	Aquatic ·species¤		
Component¤	A5¤	VEGA¤	LD50··(mg/kg)¤	LC50·(mg/L)¤		EC50·(mg/L)¤	
Alumina¤	α	α	>.5000 (oral, rat)¤	>.2.3.(4h, inhalation, rat)¤	>·218.64·(96h, fish)¤	α	
Aluminium¤			2000⋅mg/kg⋅(oral,⋅rat)¤	Ω	α	1,5 (algae)¤	
Ammonium perchlorate¤	α	α	1900 (oral, rat)¤	α	α	2 (bacteria)¤	
Antimony trioxide Sb2O3¤	α	α	34600 ·(oral, ·rat)¤	α	> 1,000 (96h, fish)¤	>1,000 (daphnia magna)+ 67 (algae)¤	
Antimony¤	¤	n	7 (oral, ∙rat)¤	n	261 (24h, larvae)¶ 4.92 (24h, flea)¶ ·206 (72h, algae)¤	۵	
Aramid·fibre¤	α	α	7500 (oral, rat)¤	α	¤	α	
Bentonite¤	α	α	35 (intravenous, rat)¤	α	19000 (96h, fish)¤	α	
BeO (beryllium oxide)¤	α	α	2062 (oral, mouse)¤	α	α	α	
Boron¤	α	α	650 (oral, rat)¤	α	α	α	
Bromine¤	¤	α	2.600 ·(oral, ·rat)¤	2,700 ·· (inhalation, ·rat)¤	¤	Fish·>·10·(fish)·⊷ ·10·(daphnia magna)¤	
CaCO3 (calcium carbonate)¤	Ω	α	6450 (oral, rat)¤	Ω	56.000.(48h, fish)¤	α	
Cadmium¤	n	α	2330 ·(oral, ·rat)¤	α	0,001 (96h, fish)¤	0.024 (daphnia magna)⊷ ·0.023 (algae)¤	
Ceramic¤	Ω	α	>22,500 (oral, rat)¤	¤	>·10·000·(72h, fish)¤	α	
Chlorine¤	n	a	α	293 ppm (1h, inhalation,	0.014-(96h -fish)α	0 019-(danhnia-maona)¤	
	i	i				 	

# (Eco)Toxicity of launcher components

Our study showed that

- There were 30 substances from the launchers with no quantitative toxicological information available.
- There are 48 substances from the launchers with no quantitative ecotoxicological information available.
- There are 26 substances for which there are neither toxicological nor ecological quantitative information available
- For the two launchers, the top 5 of the most risk substances were : paint, chlorine, cadmium, copper, zinc

Alumina, mercury, ethylbenzene, nickel, sulphur are also part of the substances that can pose the highest risks to the marine environment

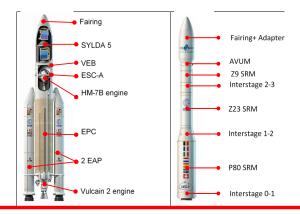












# Metallic compounds



Literature review Model experiments in laboratory conditions On-site studies in French Guyana



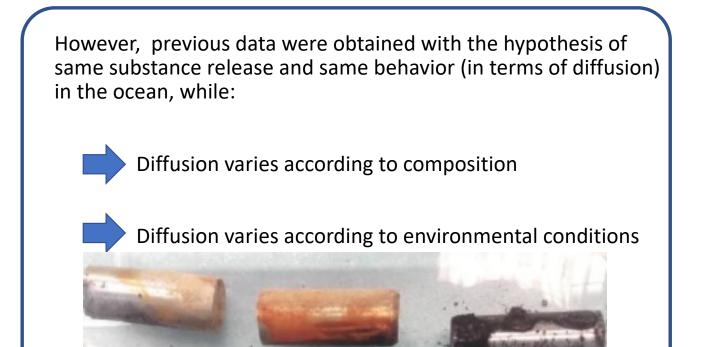








# **Toxicity** of components of launchers in marine conditions is function of their composition and behavior







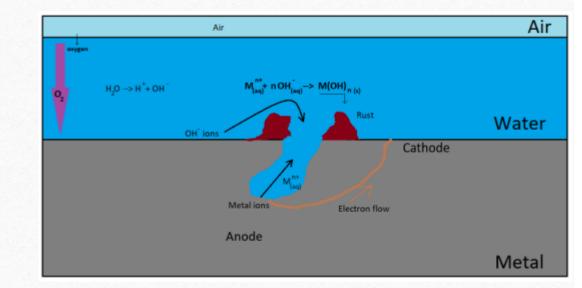






# REACTIVITY =f(environmental conditions)

- oxydo-reduction
- Influencing parameters
  - salinity
  - depth
  - pH
  - dissolved O2

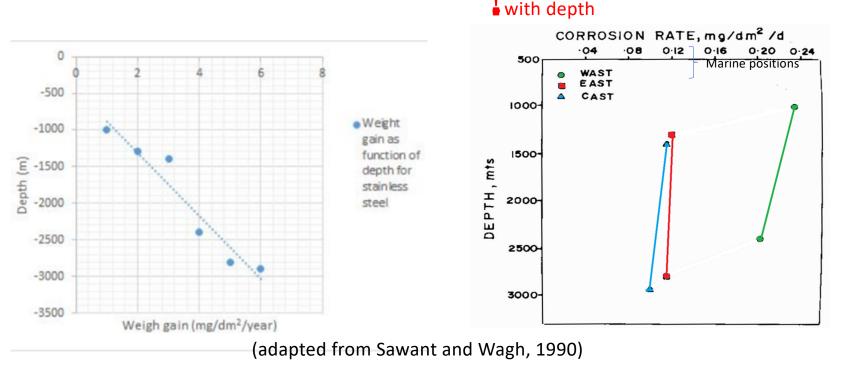


#### metal oxydation in sea water (IKM3NeT Consortium, 2012)



#### Metal corrosion as a function of depth varries with the metal

Weight gain and corrosion rates as a function of depth for various metalic alloys (adapted from Sawant and Wagh, 1990





Inverse relationship for the corrosion rate of aluminium

## Metal (bio) corrosion in sea water = f ( compounds composition)

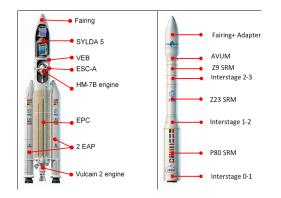
metal	corrosion product in sea water	References
Fe	FeS ; Fe <sub>2</sub> O <sub>3</sub> ; Fe <sub>3</sub> O <sub>4</sub> ; Fe(OH) <sub>2</sub> ; Fe(OH) <sub>3</sub>	Lee et Al. (2013)
		Byrne & Kester (1976)
Al	Al <sup>3+</sup> <sub>(aq)</sub> ; Al(OH) <sub>4</sub> (aq); Al(OH) <sub>3(aq)</sub> ; Al(OH) <sub>2</sub> (aq);	Sherif (2011)
	AlO <sub>2 (aq)</sub> ; Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3(s)</sub> ; Al <sub>2</sub> O <sub>3(s)</sub> ; Al(OH) <sub>2</sub> Cl <sub>2</sub>	Wharton et Al. (2005)
Ti	TiO; TiO <sub>2</sub> ; TiO <sub>3</sub> ; TiO <sub>x</sub> N <sub>y</sub> (TiN)	Totolin et Al. (2016)
Cu	Cu₂O ; CuO	Wharton et Al. (2005)
Cr	$Cr^{3+}$ ; $Cr(OH)_{2^{+}}$ ; $Cr(OH)_{3}$ ; $Cr(OH)_{4^{-}}$ ; $HCrO_{4^{-}}$ ; $CrO_{4^{2^{-}}}$ ;	Van der Weijden & Reith (1982)
	Cr <sub>2</sub> O <sub>3</sub>	Fukai (1967)
		Nakayama et Al. (1981)
V	VO <sup>2+</sup> ; H <sub>3</sub> VO <sub>4</sub> ; H <sub>2</sub> VO <sub>4</sub> <sup>-</sup> ; HVO <sub>4</sub> <sup>2-</sup> ; VO <sub>4</sub> <sup>3-</sup> ; VO <sup>2+</sup>	Nukatsuka et Al. (2002)
Ni	Ni <sup>2+</sup> ; NiO	Van den Berg et Al. (1987)
		Gong et Al. (2011)
Zr	ZrO <sup>2+</sup>	McKelvey & Orians (1993)
Mg	Mg(OH) <sub>2</sub> ; Mg <sup>2+</sup> ; MgO	Zou et Al (2011)
		Pardo et Al. (2008)
Со	Co <sup>2+</sup>	Ellwood & Van den Berg (2001)
sa	UNIVERSITÉ DE MONTPELLIER	Deloitte. museum







# Experimental set-up



- metallic corrosion in seawater and toxicity were followed in a range of conditions for a set of representative alloys used in aerospace vessels
  - Experimental set ups were designed for a set of representative metal components of VEGA and & ARIANE LAUNCHERS
  - Follow-ups were performed in representative ecosystems (French Guyana)











## EXPERIMENTAL SET UP

- stainless steel and carbon steel
- sterile and non-sterile sea water
- 3 conditions
  - aerobiosis
  - anaerobiosis
  - interface















# Selected steels

#### X15TN (stainless steel)

Witness

35NCD16 (carbon steel)

component of launchers



15CDV6 (carbon steel)

component of launchers



#### **CHEMICAL COMPOSITION**

	С	Si	Mn	Cr	Мо	v	N	Ni
min.	0.37	-	1.01	15.00	1.50	0.20	0.16	
max.	0.45	0.60	0.60	16.50	1.90	0.40	0.25	0.30

#### COMPOSITION -

Carbone	0,15
Chrome	1,25
Molybdène	0,90
Vanadium	

#### COMPOSITION

Carbone0,35
Nickel
Chrome1,70
Molybdène0,30

## Experimental set- up

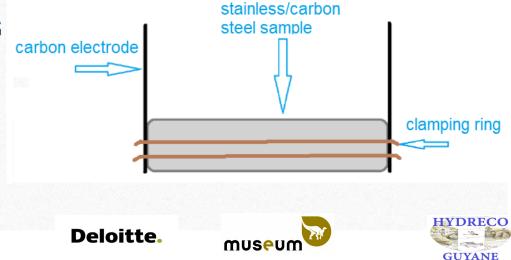
pH follow-up

esa

- measures of electric potential
- measures of sample weigth
- electron microscopy observations
- ICP-MS elemental analysis
- ecotoxicological follow up



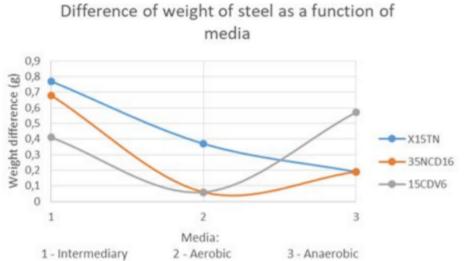




Metal corrosion as a function of composition and marine oxygen level

• Corrosion in seawater estimated from weight in aerobic, anaerobic and mixed conditions (our work, unpublished results)

Steel		Weight before	Weight after	difference	
	Tank 1	120,36	119,59	0,77	0,9
X15TN	Tank 2	120,05	119,68	0,37	8,0 g 0,7 e
	Tank 3	120,08	119,89	0,19	u 0,6
	Tank 1	122,88	122,2	0,68	0,5 0,4
35NCD16	Tank 2	123,66	123,6	0,06	Weight 0,3 0,1 0,1
	Tank 3	122,89	122,7	0,19	₩ 0,2 M 0,1
	Tank 1	122,7	122,29	0,41	0
15CDV6	Tank 2	122,44	122,38	0,06	
	Tank 3	122,56	121,99	0,57	1





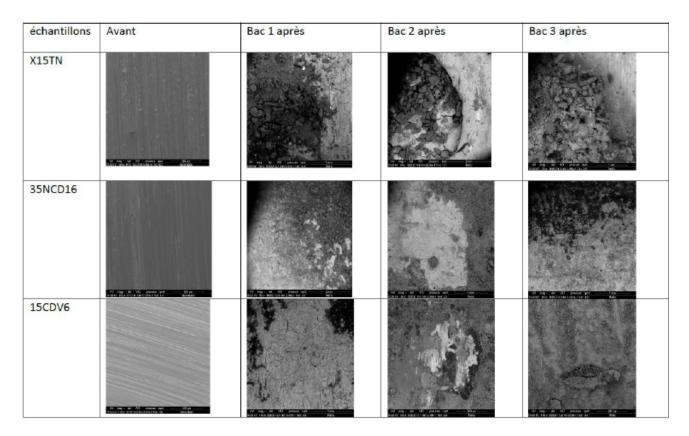






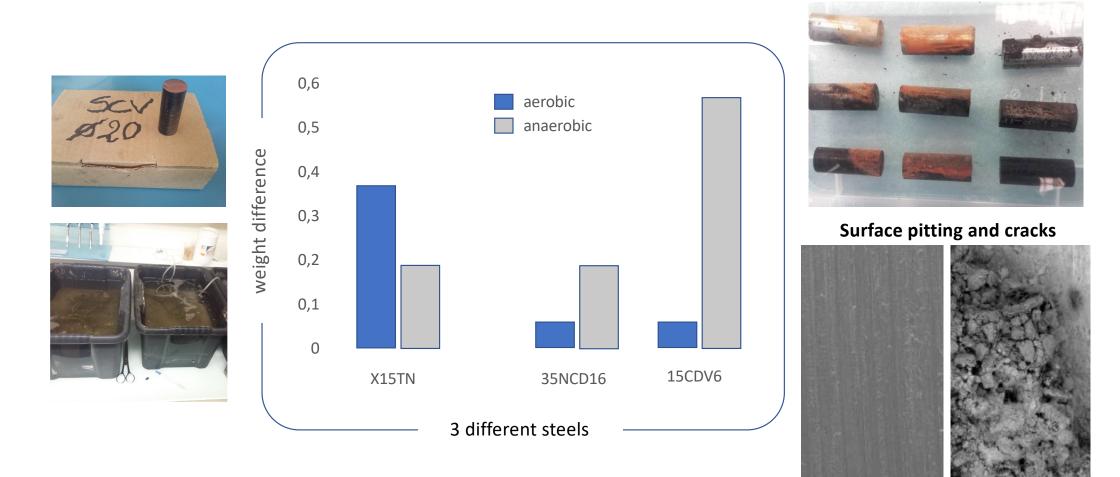


# MEB analysis confirmed that (bio) corrosion depends on conditions



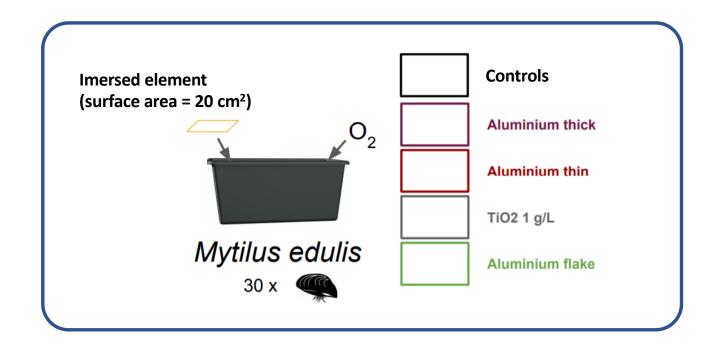
#### Metallic corrosion as a function of metallic composition and seawater oxygen level

Corrosion in seawater estimated from weight in aerobic & anaerobic conditions



#### Ecotoxicity evaluation

#### Macrofauna in vitro





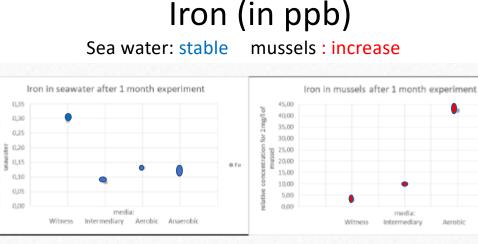








# Metal analysis (after 1 month) in sea water and mussels

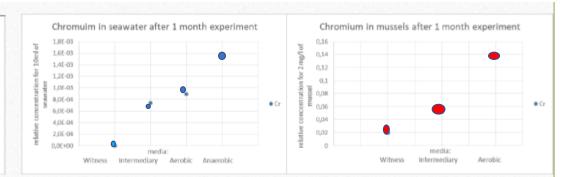


Graphiques représentants les concentrations en (ppb) de Fer dans l'eau de mer et dans les moules après un mois d'expérimentation.

# Chromium (in ppb)

Sea water: increase

mussels : increase



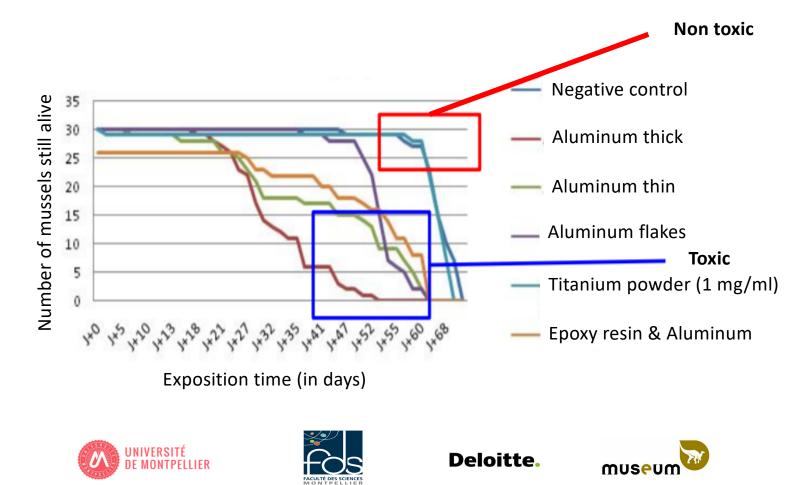
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#### Ecotoxicity evaluation

#### Macrofauna in vitro

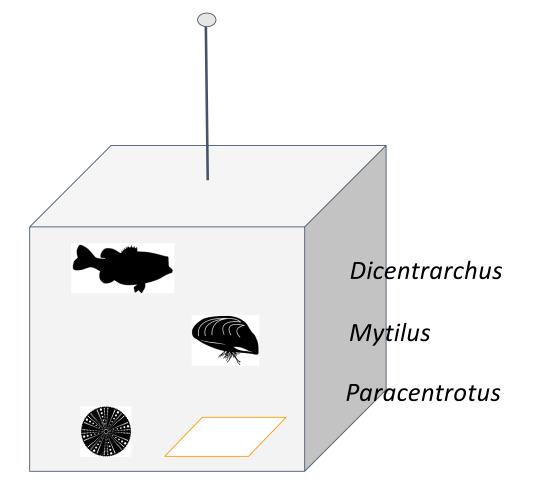
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Survival curve for mussels exposed to different metals





# Ecotoxicological 'in situ' assessements



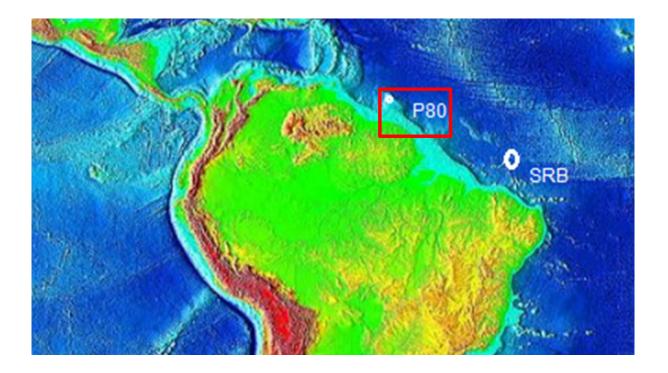


# **IN SITU IMPACT STUDIES in French** Guyana





# Ecotoxicaligal assessments near French Guyana first stage falling point













#### **IN SITU IMPACT STUDIES in French Guyana**

Sediment status

# In some locations, aluminum concentrations are high

September 2014 60 Haut Passoura Karouabo Amont Passoura aval 50 mg/Kg MS g/Kg MS 40 Anthropogenic contaminations ? 30 20 10 0 18 20 10 60 CA CD MD 4 Ø 4 2º se 0 ¢¢ 15 HYDRECO UNIVERSITÉ DE MONTPELLIER **Deloitte.** esa museur **GUYANE** 

#### **IN SITU IMPACT STUDIES in French Guyana**

#### - Water Quality

- Turbidity, Ph & Conductivity values are low
- Clear waters
- Physico-chemical characteristics of the environment change according to the season

#### Fish populations

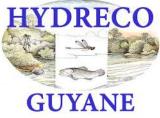
- Sites in good environmental health
- Strong imbalance in local fish population distribution (Vigouroux & Guillemet, 2006)

50,0 45.0 40,0 35,0 30.0 Karouabo Amont 25.0 Passoura Amont 20.0 Passoura Aval 15,0 10,0 5,0 0.0 pH (u.ph) Т°С  $C(\mu S/cm)$ 02 mg/l Turbidité

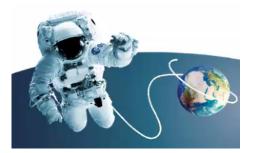
However, the successive launches of Ariane can induce the release of various products into the environment (including aluminum), with potentially a non-negligible impact on fish



In situ measurements



NTU





## **Conclusions & Perspectives**











# **Conclusions & Perspectives**

- Behaviour and toxicity of the different compounds carried out varry according to the substrate but also to environmental conditions (depth oxygen availaibilities)
- Exposure time must be taken into consideration and no 'rapid' conclusion can be driven from the available litterature
  => experimental approach used during the project
- Longer impacts need to be investigated



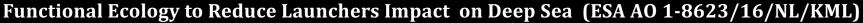














# Thank you for your attention !

UNESCO and France have formalized the creation in Montpellier of the International Centre for Interdisciplinary Research on Water Systems Dynamics (ICIReWaRD) which will provide expertise, carry out research and training actions in management and governance, of water science and technology in vulnerable regions, focusing in particular on problems linked to rapid urbanization, demographic pressure and the foreseeable effects of climate change.



















