The 6th Harsh-Environment Mass Spectrometry Workshop
September 17-20, 2007 Cocoa Beach, Florida

Short-term Oxidation-Reduction processes in a hypoxic estuary by means of an *in situ* Mass Spectrometer

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Summary

1. Introduction
2. Methods
3. Results
4. Conclusions

INTRODUCTION

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Bilbao

San Sebastián

- Founded in1981
- Non-profit private Technological Center
- Specialized in Marine and Food Research
- Facilities in Bilbao and San Sebastián
- Delegations in Madrid, Argentina, Ecuador and Chile

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- One of the main areas of AZTI's Marine Research Division is the management of the marine environment.
- Monitoring and environmental quality control of coastal and estuarine waters of the Basque Country is carried out since 1995, in order to assess the Ecological Status of water masses
- The most advanced specialised devices in marine research (CTDs, current meters, tide and wave gauges, multibeam, etc.) are used.
- Recently, we have purchased a portable underwater mass spectrometer able of measure volatile organic compounds and dissolved gases related to biogeochemical processes.

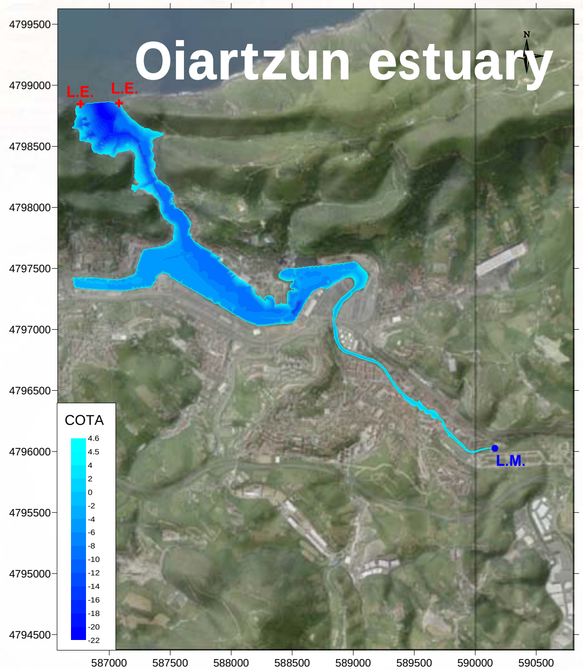
Objectives

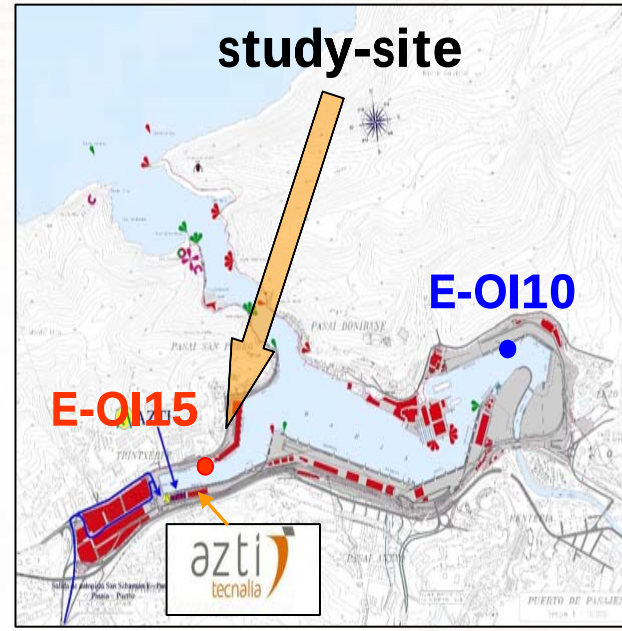
Hence, our main objective in this contribution is to **check and compare, classical oceanographic monitoring data** with data obtained using an **in situ underwater mass spectrometer**, studying problems and complementarities associated to both methodologies





The Site





Oiartzun river estuary: The 2nd Commercial Harbour of the Basque Country.

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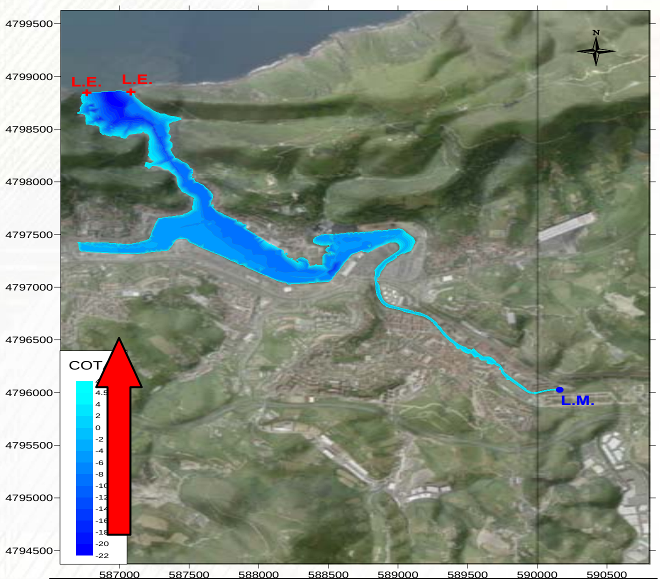
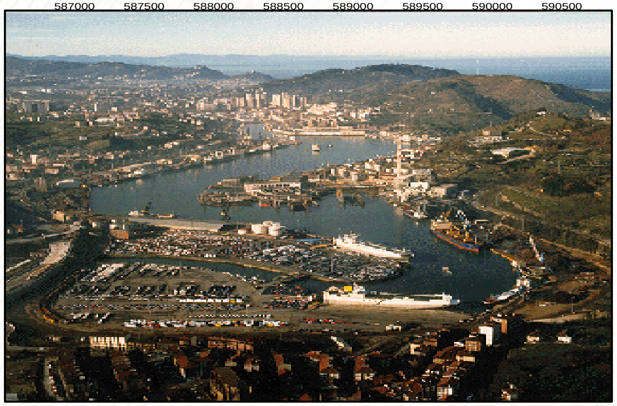
The Site





- ➢ Special morphology (small fjord-like estuary)
- ➢ Strongly modified for navigation purposes

- ➢ Small river basin and river flow vs. relatively high estuarine volume.

- ➢ Mesotidal (≈ 2-4 m of tidal amplitude) but high residence times of the water masses, specially for the secondary segments.

- ➢ Heavily inhabited and industrialised
- ➢ Strong environmental pressures
- ➢ Multiple subsequent impacts

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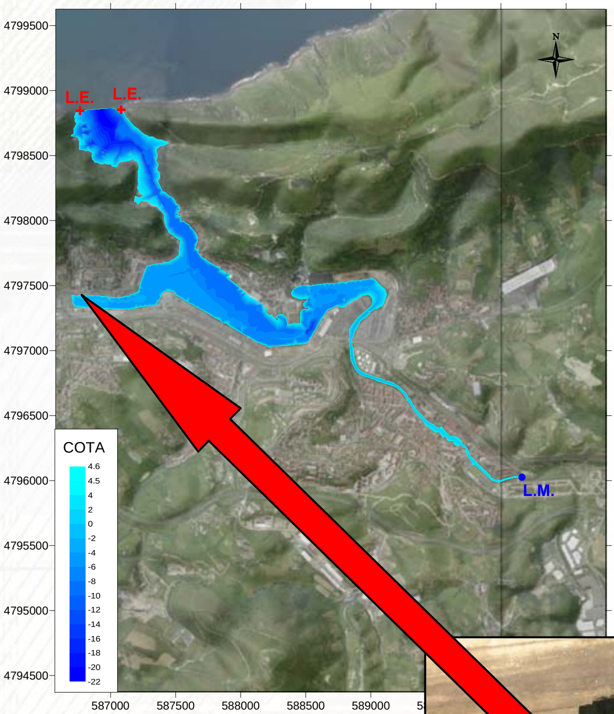
The Site/ The Processes



- On going (but incomplete) sewage disposal
- Large loads of organic matter (now, mainly from domestic wastes) still discharged into the less renewable water segment.

- Strong and relatively fast oxygen consumption enhanced by organic matter rich, heavily reduced sediments.

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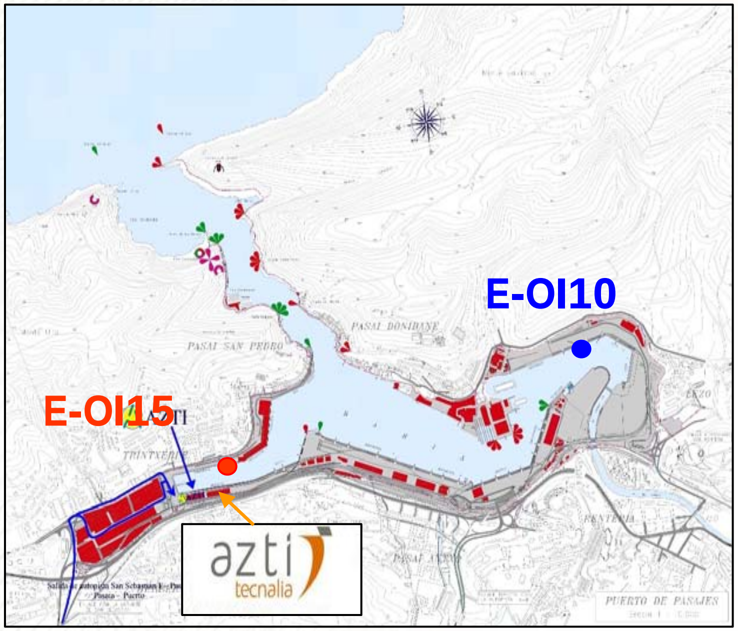
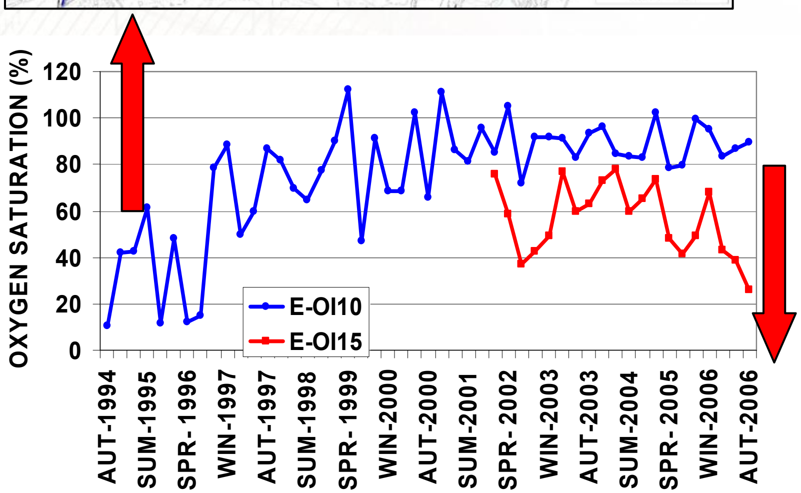
•The Site/ The Processes





- Fast reduction processes take place depending on different conditions: tidal amplitude, composition of the land runoff and wastewater inputs, etc…

•Dilution with good-quality water from other reaches is not enough.

•Events of hypoxia, denitrification and sulphatereduction are quite frequents with some reactivation (frequency and intensity) along the last two years.

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Hypothesis

- Are the concentrations of the molecular species (non ionic forms in the dissociation or hydrolisis equilibria) high enough to be detected?
- When and Where?
- Quantification or just qualitative patterns?

Can be coupled classical marine monitoring data:

- CTD continuous profiles (T, S, pH, O_2,…)
- Discrete depth water samples (NH_4^+, NO_3^-, NO_2^-, TOC…)

and UMS measurements?

If yes…

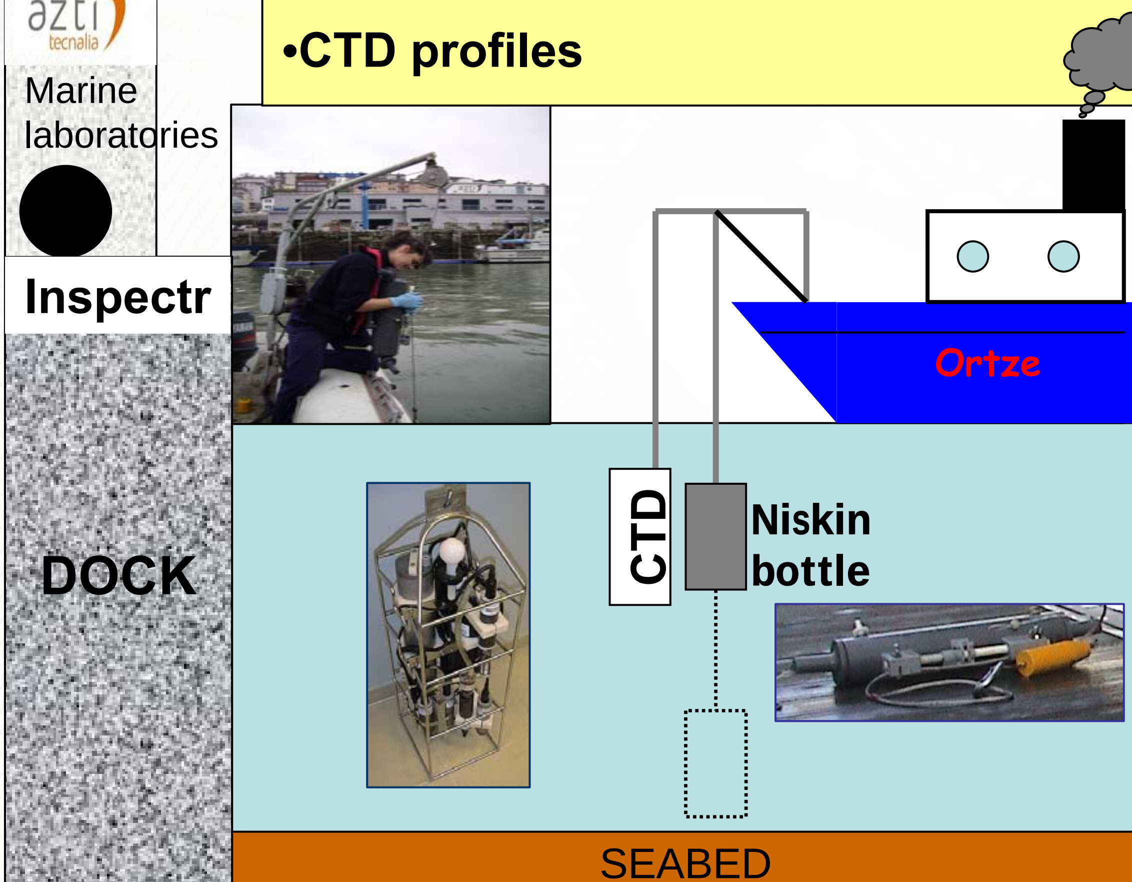
Applications for calibration/quantification of UMS data

Improved monitoring: better spatial and temporal resolution (profiling, trawling, undulating)

METHODS

Methods sampling

- Discrete surface and bottom water samples: Niskin bottle
- Semitide cycle: 7 casts one per hour (9 a.m to 3 p.m)
- CTD profiles



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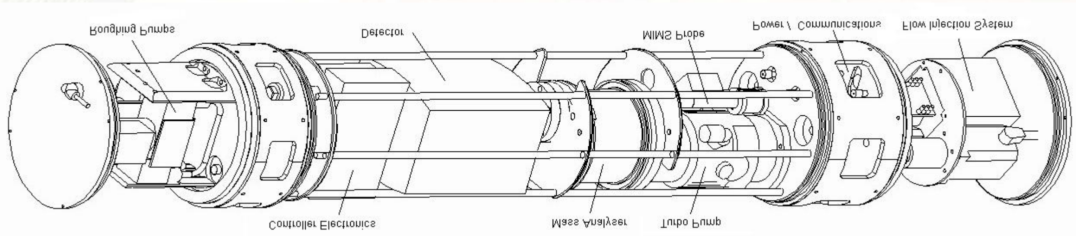
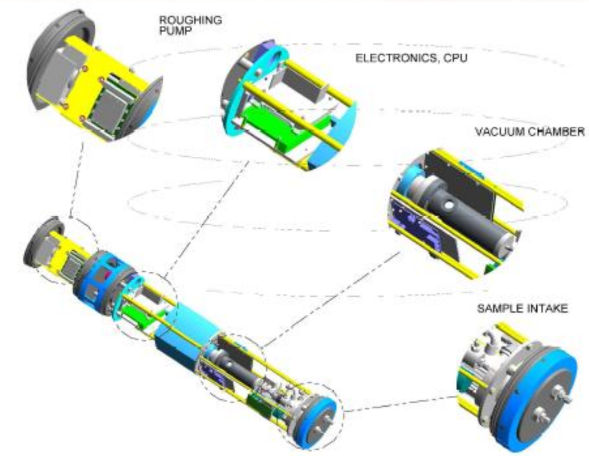
Methods classical analysis

NUTRIENTS: **Amonium, nitrate, nitrite, silicate, phosphate**	Segmented Flow Analysis (SFA) Spectrophotometric detection **µmol/L**
TOC: Total Organic Carbon	Catalitic combustion (Pt-Al2O3) in quartz tube and non-dispersive infrared detection **mg/L**
Total reduced sulphur	Spectrophotometric detection. DMPD method **µg/L**
Temperature, salinity, pH, %O2, chlorophyll, transmitancy	**CTD**: SBE 25-01 SEA BIRD 25-seaLOGGER

Methods In-Spectr

Underwater Mass Spectrometer “In-Spectr”





- **Manufactured Applied Microsystems, model developed by the University South Florida**
- **Down to 200 m water depth**
- **Measure analytes up to 200 AMU**
- **MOLECULAR dissolved gases: NH_3, O_2, CO_2, H_2S, CH4.**
- **3 pressure vessels**

Type	linear mass quadrupole
Mass range	200 amu
Inlet	Membrane PDMS
Consumption	95 W
Voltage	24 V
Dimensions	19 cm Ø, 114cm long, 33kg
Profundidad	200m max

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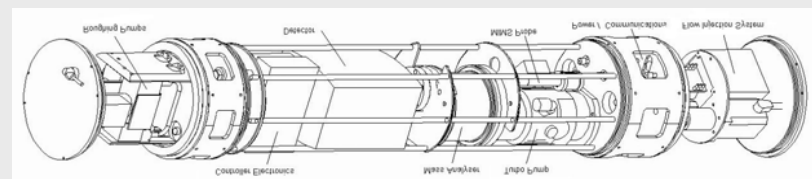
Methods In-Spectr

Underwater Mass Spectrometer “In-Spectr”

- Discrete seawater samples were analysed, inserting deionized water between samples.
- Firstly surface water and then bottom samples in chronologically order.
- Ions measured (m/z): 15 CH_4



16 NH_3

32 O_2

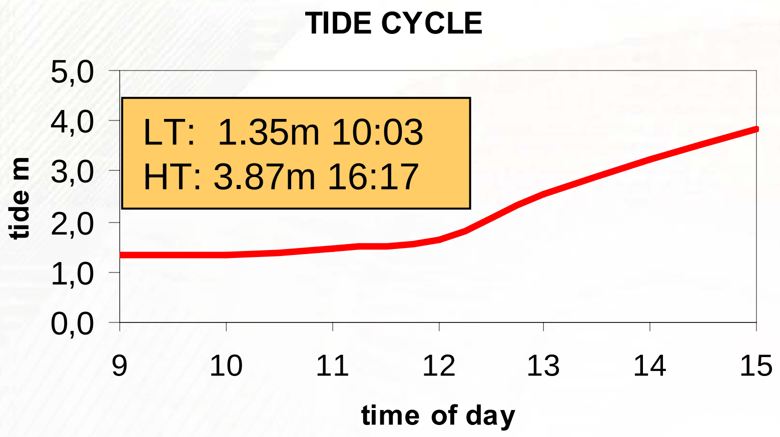
34 H_2S/O_2

40 Ar (reference/normalization)

44 $C0_2$

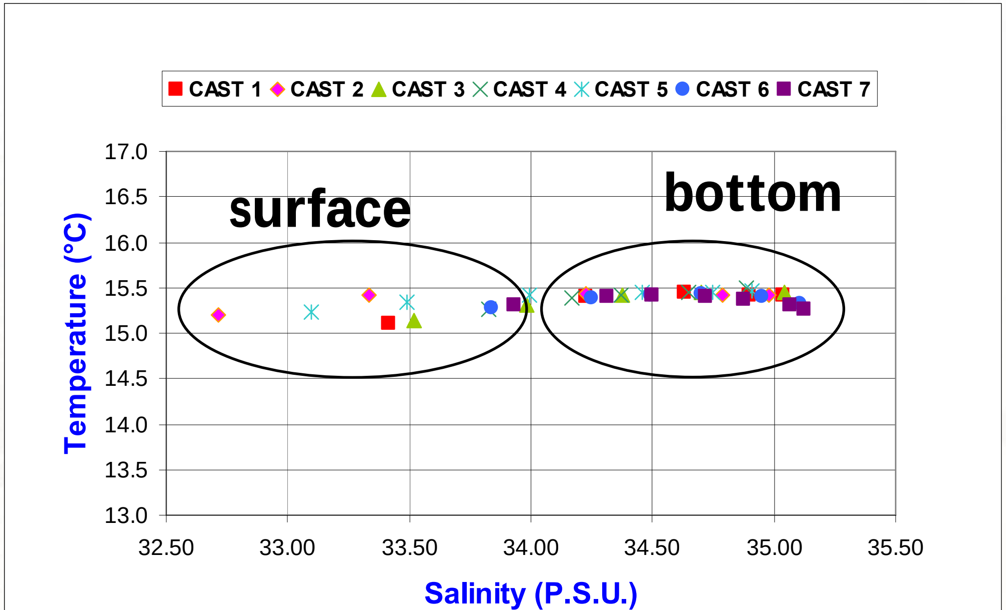
RESULTS

Results classical methods



- Neap tide (amplitude 2.52m)
- Simple mixing processes
- Duality Surface/bottom in Salinity (stratification)

TS diagram
All CTD casts



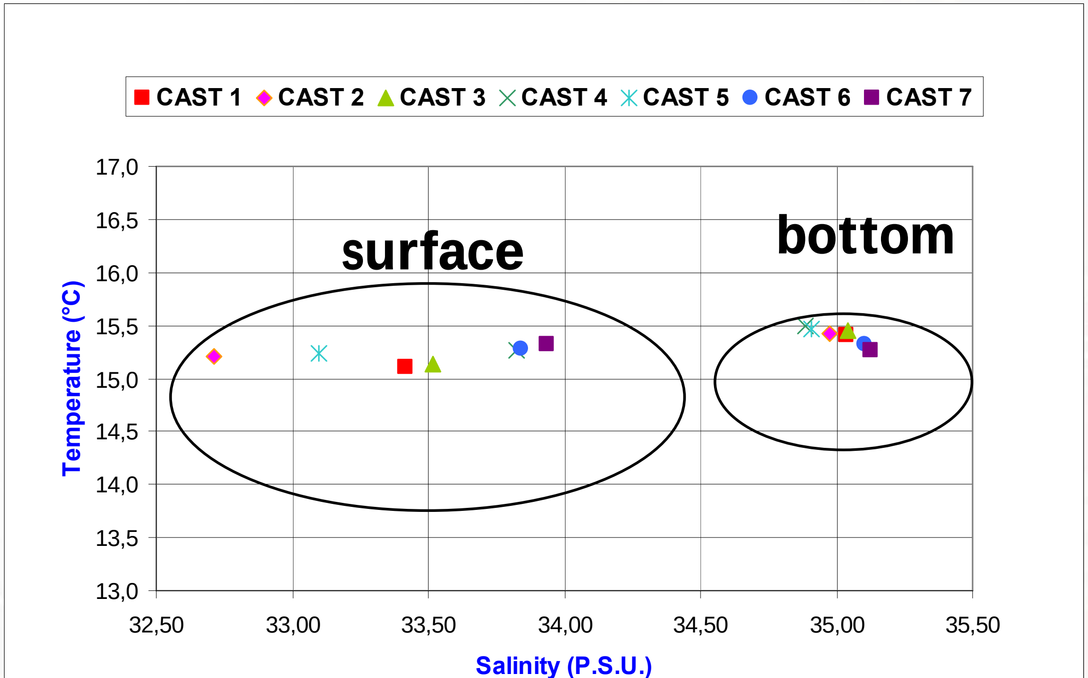
TS Diagram (all CTD Cast) (20/12/2006)

Results classical methods

		SURFACE							BOTTOM						
	time of day	9	10	11	12	13	14	15	9	10	11	12	13	14	15
m	Depth	0	0	0	0	0	0	0	4	4	4	4	5	5	6
ºC	waterT	15.1	15.2	15.1	15.3	15.2	15.3	15.3	15.4	15.4	15.4	15.5	15.4	15.4	15.3
	SAL	33.4	32.7	33.5	33.8	33.1	33.8	33.9	34.9	34.8	34.7	34.6	34.7	35.0	35.1
	Cl "a"	0.43	5.74	0.81	0.67	5.88	0.66	0.74	0.27	4.36	0.64	0.57	1.62	0.52	0.51
	pH	7.80	7.78	7.80	7.76	7.78	7.76	7.77	7.85	7.82	7.75	7.75	7.72	7.73	7.78

- **Duality Surface/bottom in Salinity (stratification)**
- **No surface sample has the same characteristics as bottom samples**

TS diagram
Niskin bottles



TS Diagram (NISKIN Bottle Samples) (20/12/2006)

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Results classical methods

		SURFACE							BOTTOM						
	time of day	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
m	**Depth**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**4**	**4**	**4**	**4**	**5**	**5**	**6**
mL/L	**O2**	1.13	0.82	0.96	0.60	0.56	0.62	0.79	1.50	0.92	1.35	0.97	0.90	1.67	1.56
	% O2	20	14	17	11	10	11	14	27	16	24	17	16	30	28
µmol/L	**Amonium**	600	550	435	415	560	515	485	29	40	42	34	62	27	44
µmol/L	**Nitrite**	8.40	10.60	8.15	11.00	13.30	13.00	15.00	1.45	1.60	1.90	1.80	2.70	1.60	1.95
µmol/L	**Nitrate**	2.05	2.70	5.85	10.85	42.00	26.00	19.00	4.15	4.75	5.75	4.95	4.55	3.15	4.20
µmol/L	**Phosfate**	72.0	48.0	32.0	31.0	68.0	47.0	42.0	2.9	3.6	3.5	2.8	4.4	2.5	3.3
µmol/L	**Silicate**	105.0	78.0	57.0	68.0	145.0	102.0	92.0	10.1	10.7	11.0	10.7	15.0	9.7	11.9

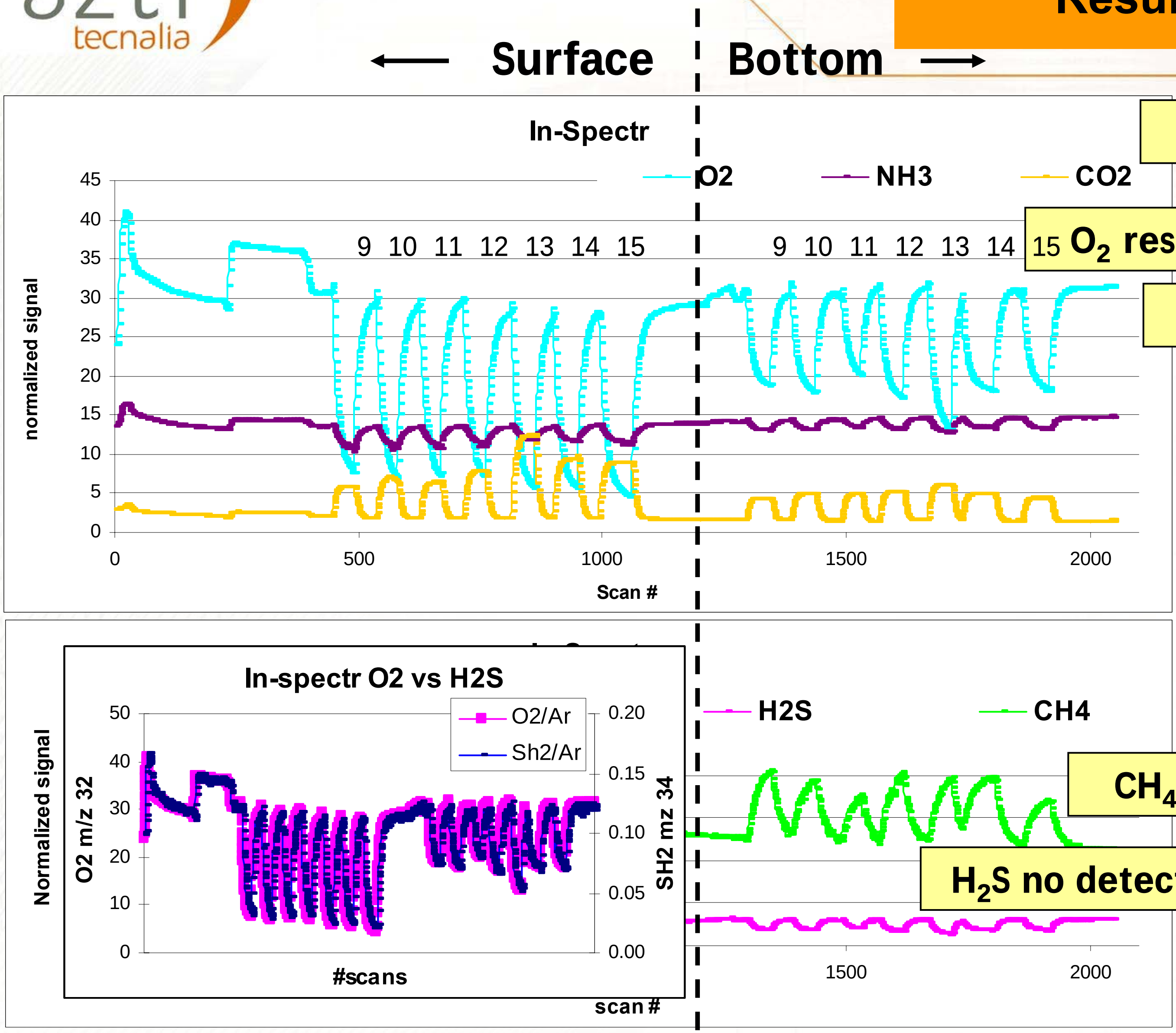
- **Severe hypoxia. O_2 saturation below 20 % in surface and 30% in bottom samples**
- **Strong O_2 demand → potential sulphatereduction**
- **Excess in ammonium and phosfate → urban wastewaters inputs**
- **Strong duality Surface/bottom**
- **Denitrification ammonium : nitrite : nitrate ratios**

Results classical methods

		SURFACE							BOTTOM						
	time of day	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
m	**Depth**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**4**	**4**	**4**	**4**	**5**	**5**	**6**
	pH	7.80	7.78	7.80	7.76	7.78	7.76	7.77	7.85	7.82	7.75	7.75	7.72	7.73	7.78
µg/L	**Sulphide**	36.8	42.4	38.2	30.0	119.0	64.6	59.2	15.6	21.0	22.4	22.4	19.0	14.6	6.8
mg/L	**TC**	61.6	53.6	48.7	50.8	80.4	64.2	60.5	28.4	28.7	47.7	28.3	31.0	48.5	26.8
mg/L	**IC**	46.4	42.9	41.9	42.0	57.2	46.4	45.0	21.7	24.9	25.0	24.4	25.6	22.9	25.9
mg/L	**TOC**	15.2	10.7	6.8	8.8	23.2	17.8	15.5	6.6	3.9	22.7	3.9	5.4	25.6	0.9

large content in total carbon (urban wastewater inputs) and total sulphides (sulphatereduction)

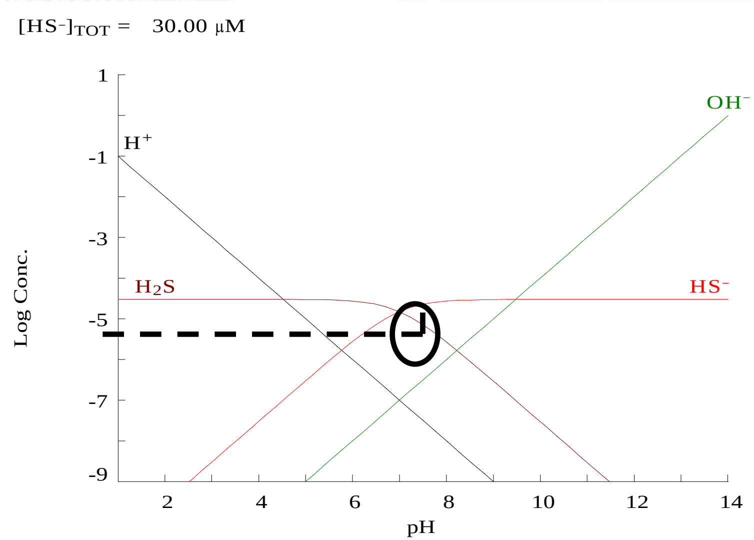
Results In-Spectr

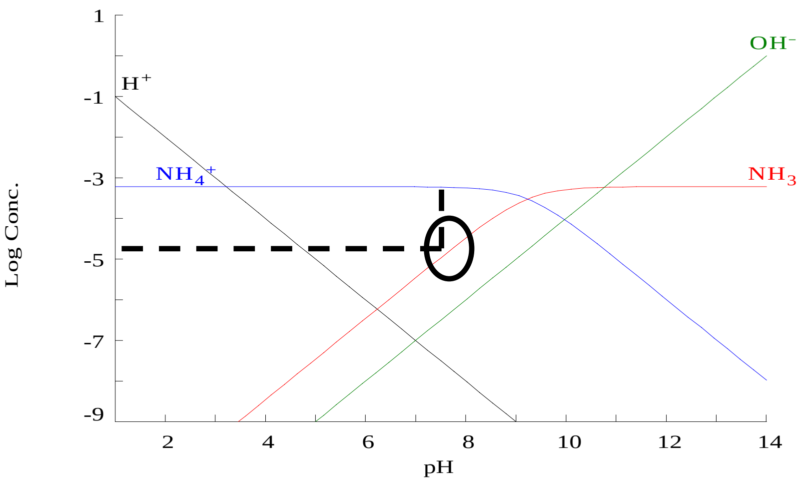


- Duality surface/bottom
- O_2 response surface <bottom
- Inverse pattern 0_2-CO_2
- CH_4 unstable signal-derive
- H_2S no detected, same pattern as O_2

Results In-Spectr

LogConc vs pH diagrams





- H_2S and NH_3 equilibra
- Concentrations by lab analysis
- pH=7.8

- Theorical concentrations

$NH_3=10^{-5}$ M detectable by In-Spectr

$H_2S=10^{-6}$ M non-detectable by In-Spectr in these conditions

CONCLUSIONS

Conclusions

- **The Oiartzun estuary is a good study-site for the investigation of fast and short-term oxidation-reduction processes**
- **Hypoxia, denitrification and sulfatereduction processes are detected by classical monitoring tools in the study area**
- **In-spectr UMS is a valuable tool for the determination of dissolved gases related to biogeochemical processes**
- **Responses in O_2 and NH_3 fit with results in classical methods and diferenciates between surface and bottom samples. H_2S could not be detected → DMS analysis instead of H_2S to assess sulphur cycle**
- **Further development is needed in laboratory: calibration and field deployment strategies**

Acknowledgements

Thank you for your attention

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