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Fate of organic priority substances accumulated in the sediment of a Mediterranean temporary river: the case of Celone stream (Puglia, Italy)

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Temporary rivers

Temporary rivers are natural water bodies that experience a recurrent dry phase of varying duration and spatial extent : they are defined as streams that are dry at least during an extended part of the year (usually summer in Mediterranean regions).

Rivers that are typically dry year-round, flowing only after rainstorms, are described as ‘ephemeral’; whereas temporary rivers that normally flow continuously during the winter are ‘seasonal’ or ‘intermittent’.

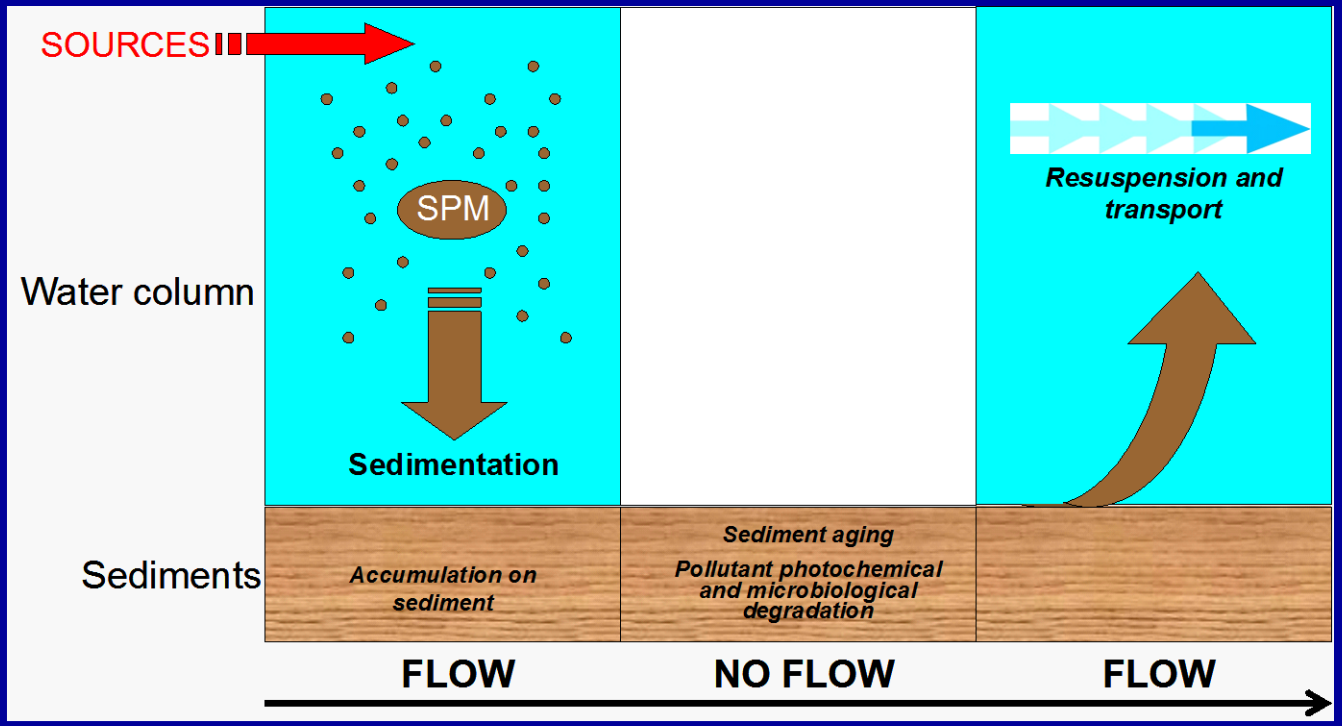
Under climate change conditions temporary rivers will be the dominant surface water bodies of the Mediterranean region.

Table 3.3: Provisional classification of stream regimes in the MIRAGE project.

stream regime	flow duration (months / year)	pools duration (months / year)	dry period (months / year)
P permanent	≥10	≤ 2	no occurrence
IP intermittent-pools	≥ 3	≤ 9	no occurrence
ID intermittent-dry	≥ 3	≥ 1	≥1
E (episodic-ephemeral)	≤ 2	variable	≥ 10

Temporary rivers

Hydrological cycle of a temporary river can be divided in three phases: i) normal flow condition, ii) dry period and iii) rapid water return with the consequent remobilisation of accumulated sediment.



What is the fate of hazardous substances under these hydrological conditions?

Fate of hazardous substances in temporary rivers

- **It is needed to understand the processes active during the dry phase on sediment.**
  - **Drying seems to hinder the aging process reported for saturated sediment**
  - **Surface drying reduces the emission rate of organic compounds adsorbed onto soils and exposed sediments.**
  - **Because dried sediment is directly exposed to solar radiance degradation of photosensitive compounds should be enhanced.**

- **The processes during the dry phase have an important influence on the mobility and availability of hazardous substances.**
  - **An increase in the leachability of metals has been shown to occur during the drying of contaminated sediments**
  - **An increase in the chemical extractability and biological availability of previously sequestered organic contaminants has been shown to occur in soil and sediment subjected to wetting and drying cycle**

- **For this reason in temporary rivers loss of moisture content in the sediment during drying phase may lead to the release of dissolved organic and metal contaminants in peak loads at the beginning of the flood.**

The EU-FP7 MIRAGE project

This work has been carried out in the framework of the EU-FP7 research project MIRAGE (Mediterranean Intermittent River ManAGEment) which aims to provide specific key knowledge for a better assessment of ecological ecological status in Mediterranean temporary streams.

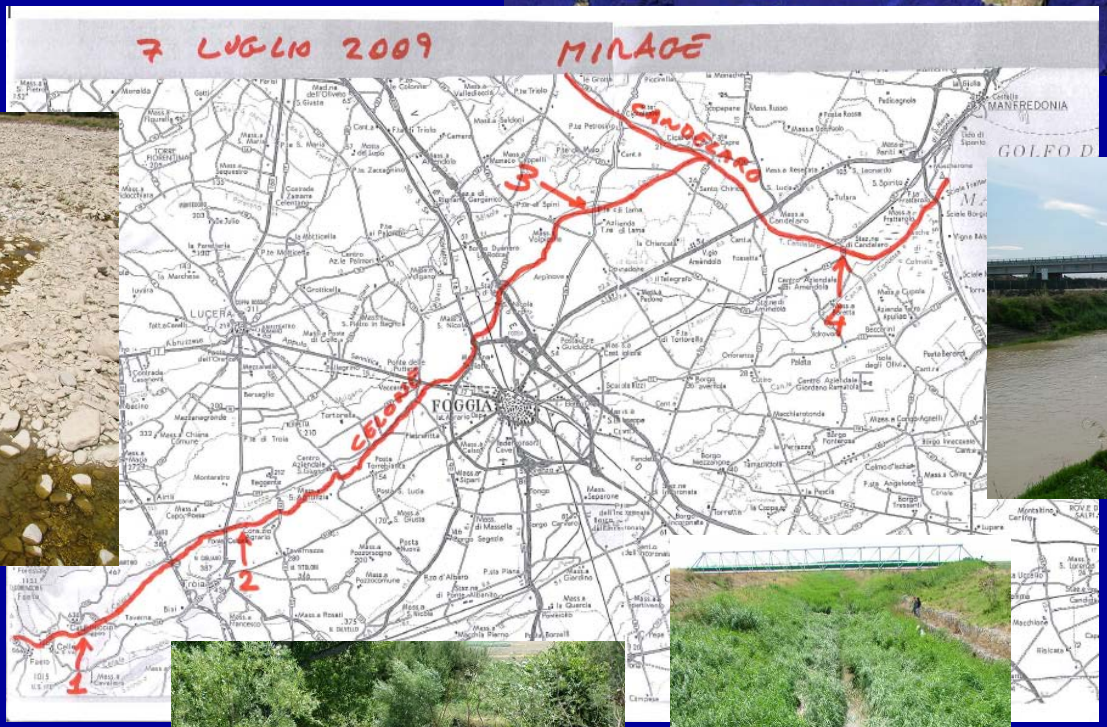
WP7 “Hazardous Substances”

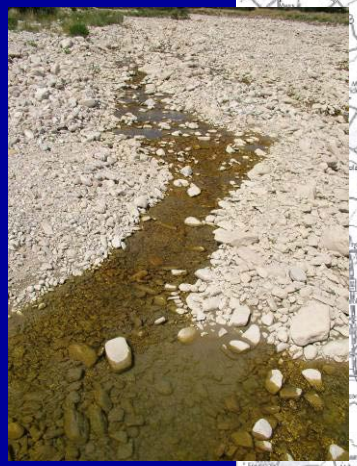
actions:

1. assess presence and distribution in water and sediments of selected h.s.
2. retrieving pollution sources from analytical data & land use
3. understanding main mechanisms affecting h.s. persistence and fate
4. provide information to tune chemical status assessment procedures and reduction measures with respect to the specificity of temporary rivers

Study Area

Celone stream in the Candelaro river basin (Puglia, Southern Italy)





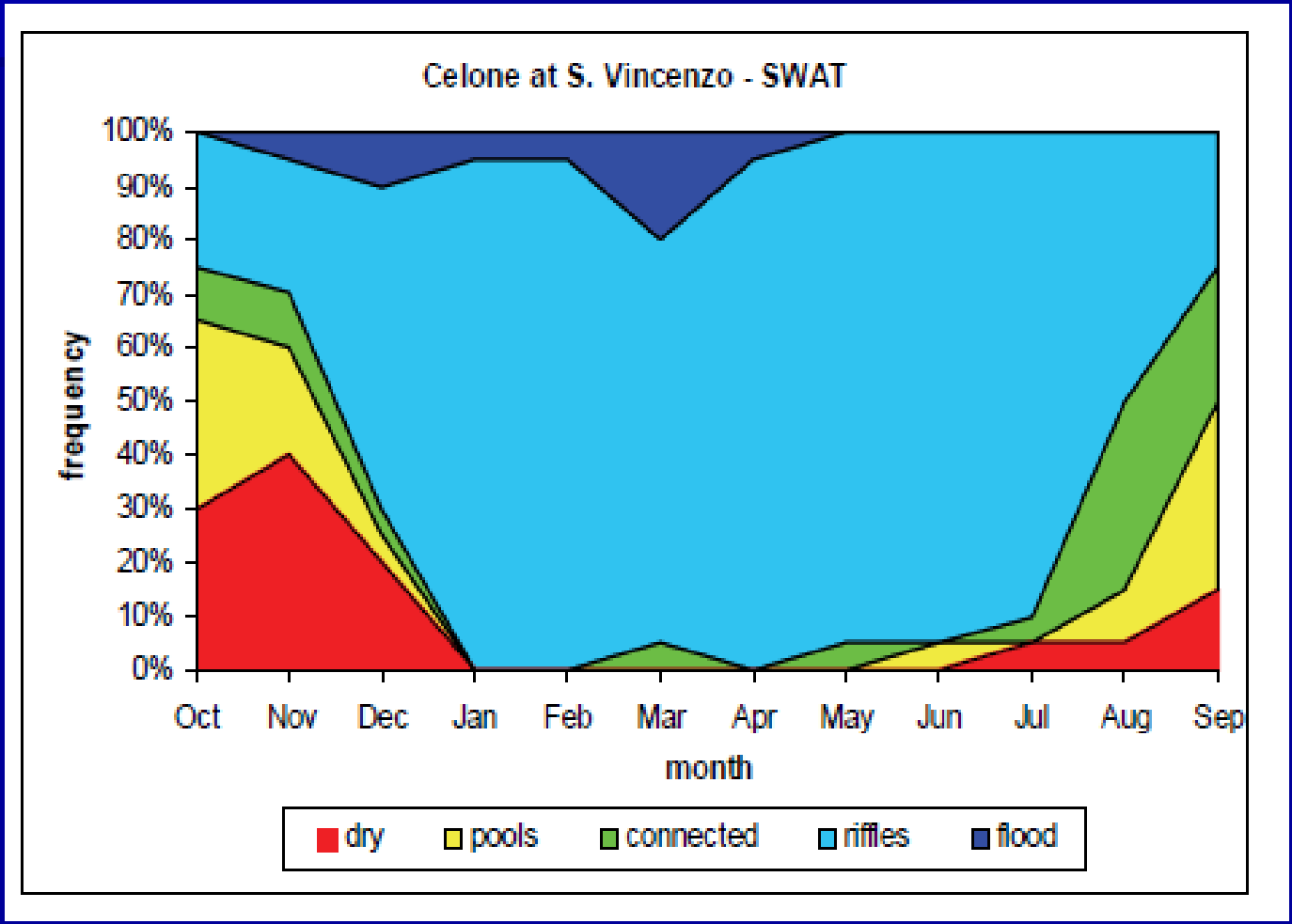
Site 1

Site 4

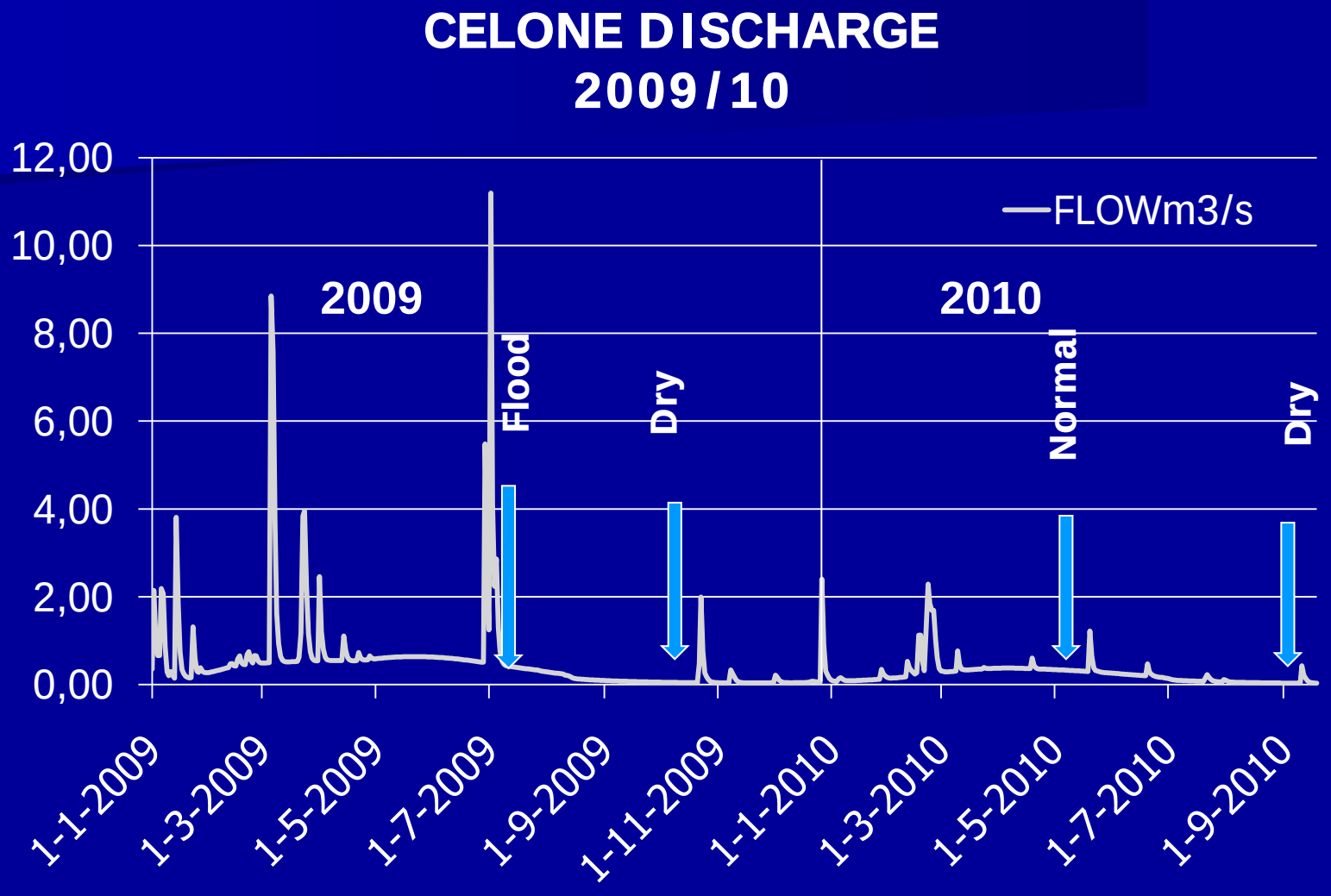
Site 2

Site 3

Hydrological characteristics of the studied basin



Sampling campaigns



2009: no dry period: flooding pulse in July normal flow; October low flow
2010: May normal flow; August dry period; September/October no flooding pulse

Analysed substances

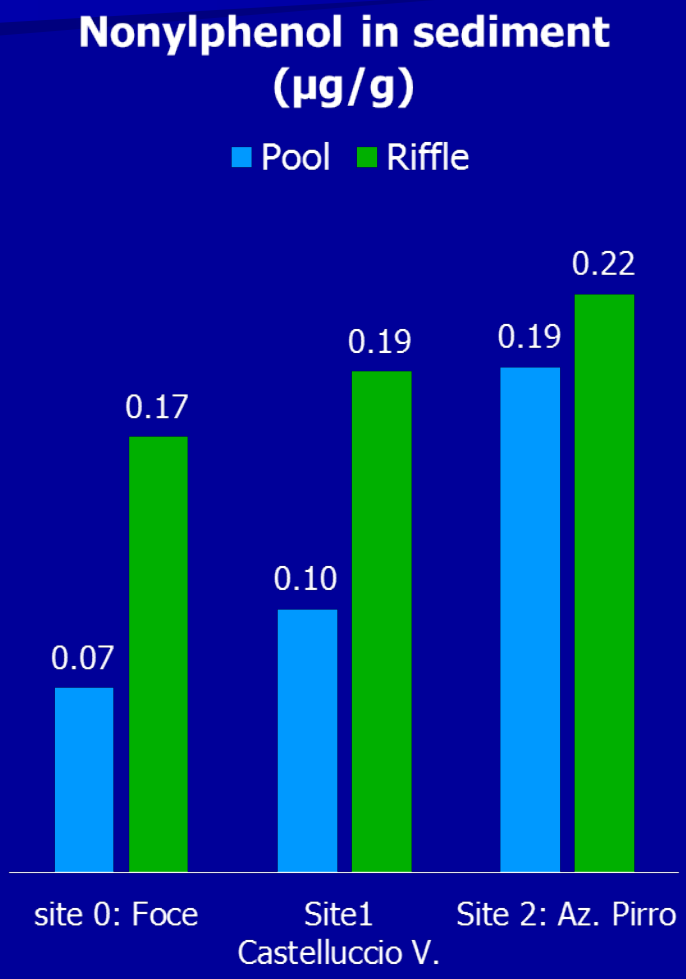
2 classes of compounds included in the WFD list of *priority hazardous substances* were monitored:

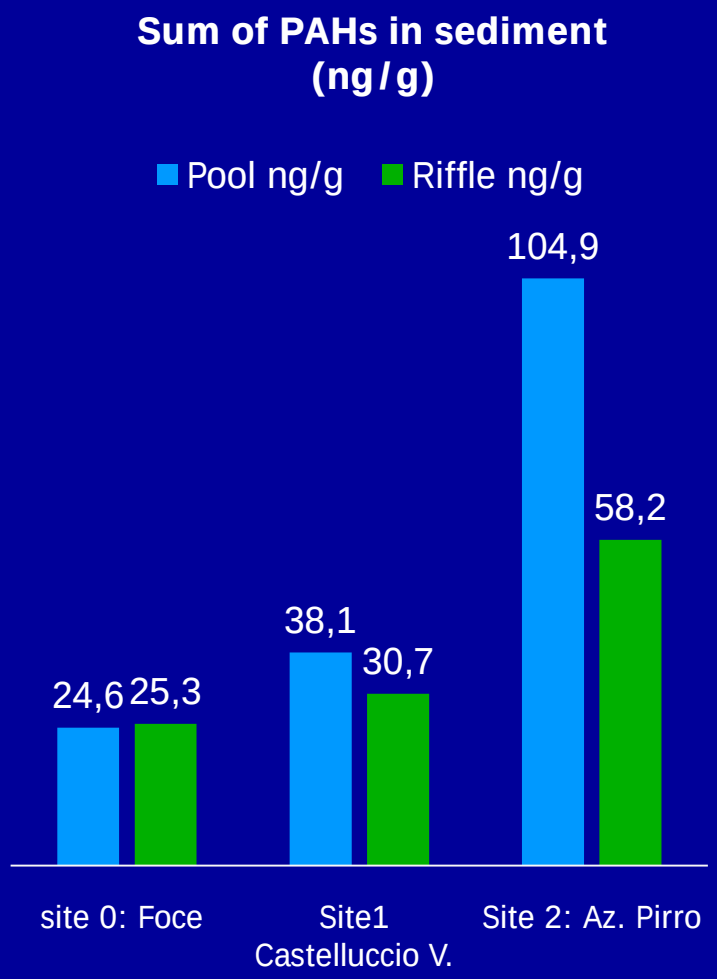
- **Alkylphenols: octylphenol, nonylphenol, nonylphenol-mono and di-ethoxylate**
  (Log K_{OC} = 4.52-4.78)

- **13 PAHs : 2 rings: Naphtalene; 3 rings: phenantrene, anthracene; 4 rings: fluoranthene, pyrene, benzo(a)anthracene, crysene; 5 rings:benzo(a)pyrene, benzo(k or b)fluoranthene, dibenzo(a,)anthracene; 6 rings: indeno(1,2,3-cd)pyrene, benzo(ghi)perylene**
  (Log K_{OC} = 4.31-6.02)

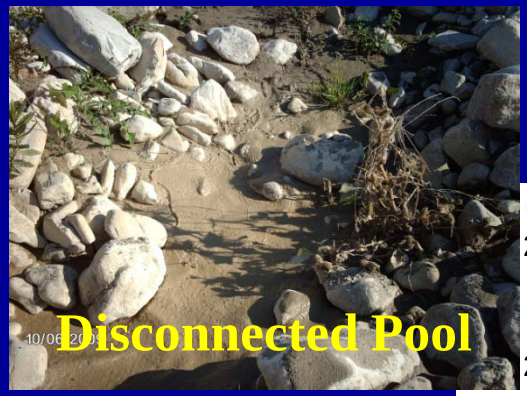
Analytical methods: Soxhlet or SPE extraction and HPLC-fluorimetry separation and determination

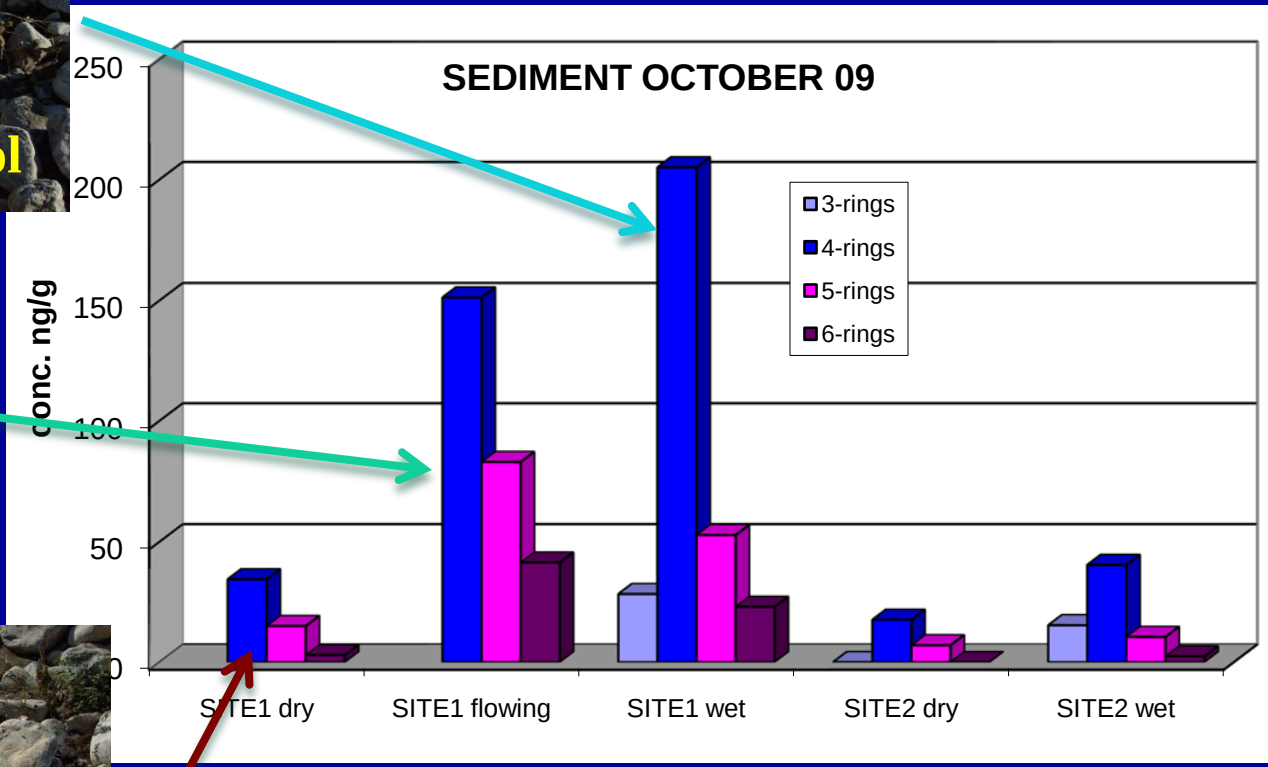
Deposition and adsoption on sediment under normal flow regime (May 2010)





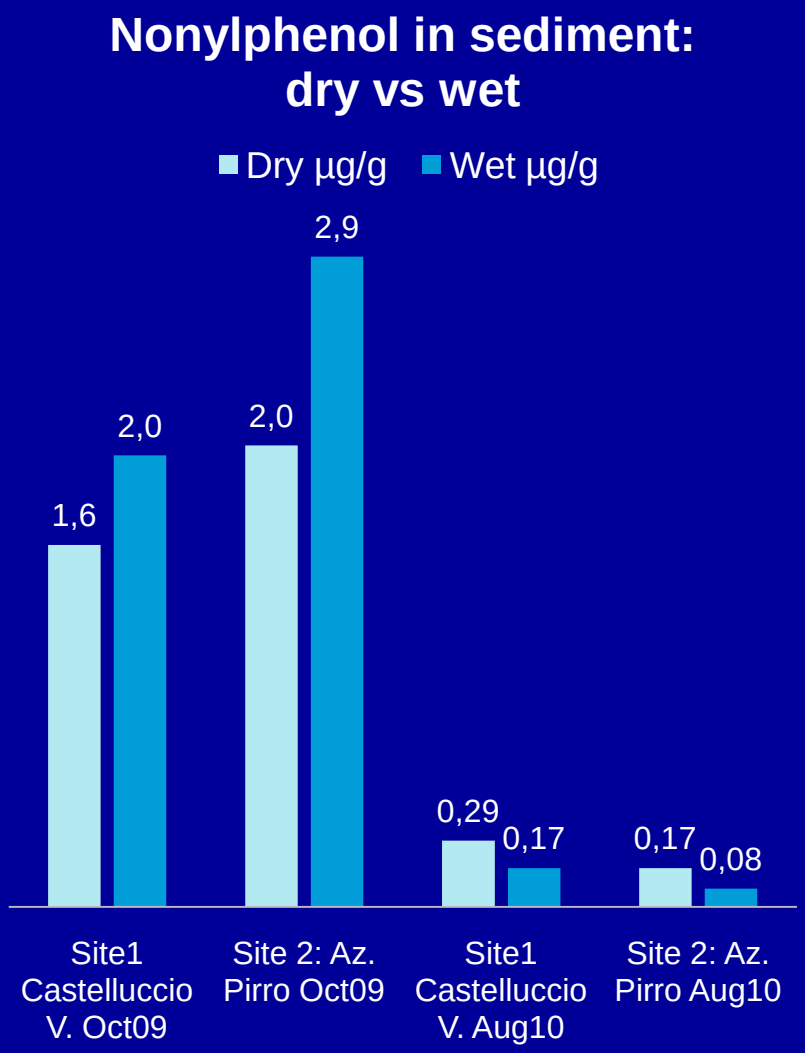
Effects of drying processes of natural sediments on PAH concentrations: October 2009

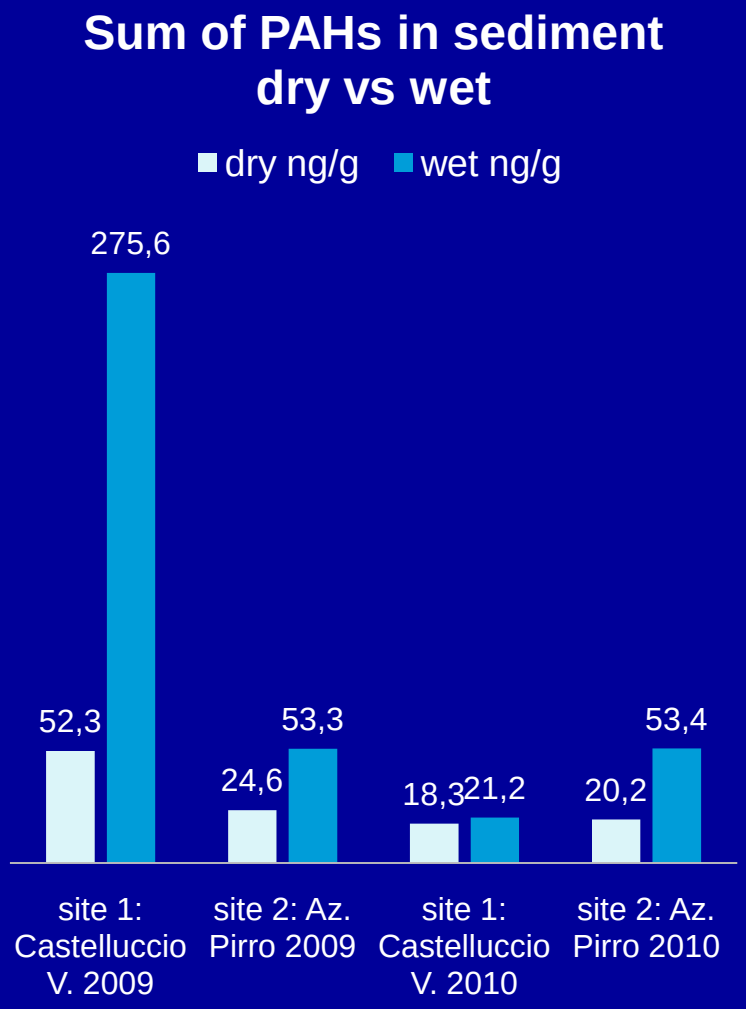




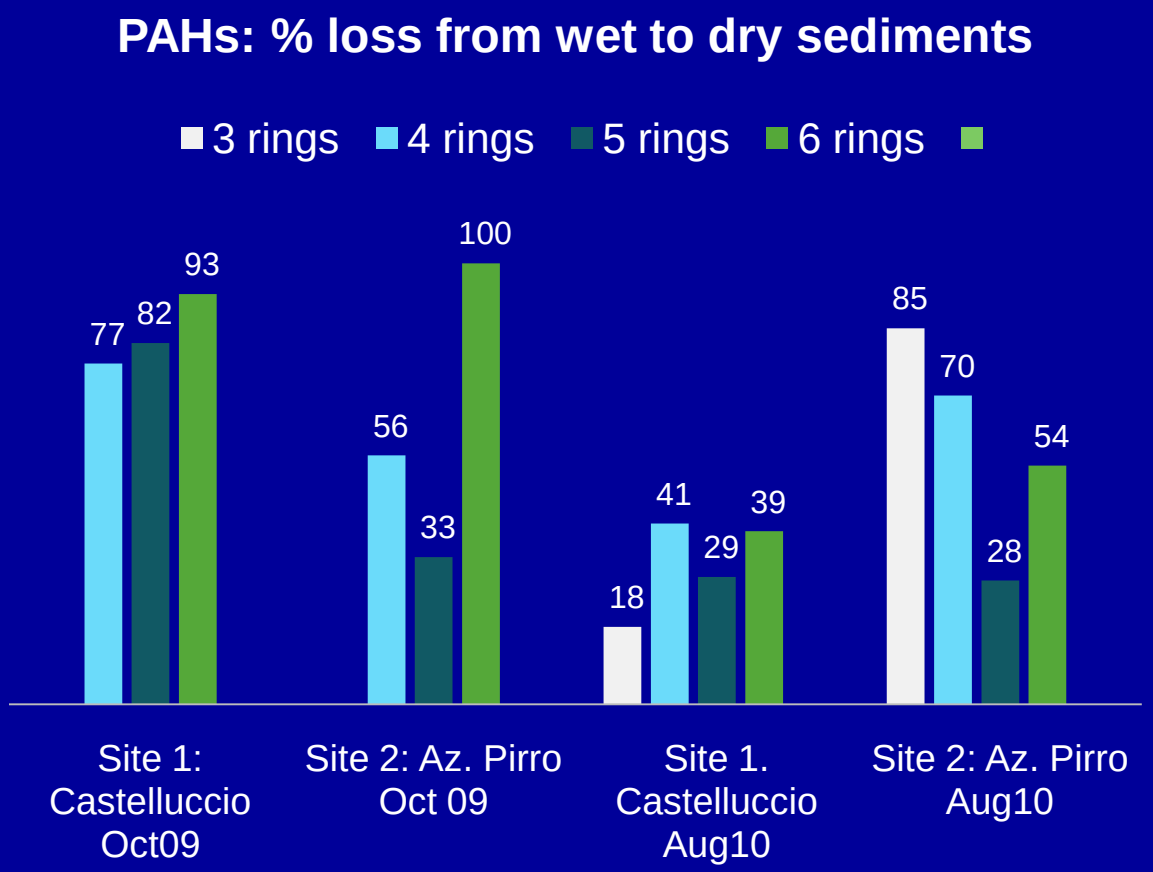
PAHs increase from riffle to disconnected pool and then decrease during drying

Dry vs wet concentrations in sediments



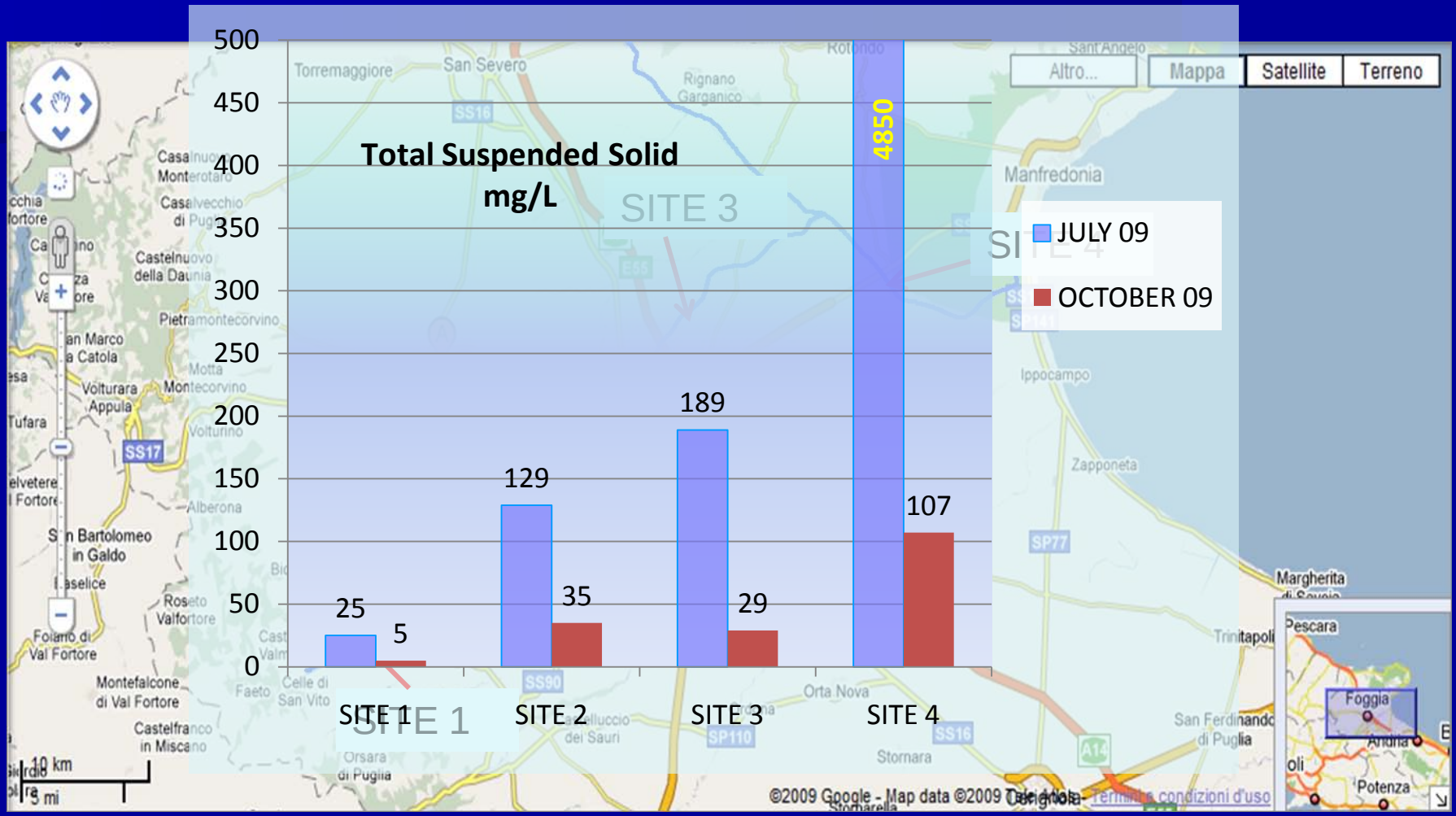


Understanding the mechanism of organic substances loss during sediment drying



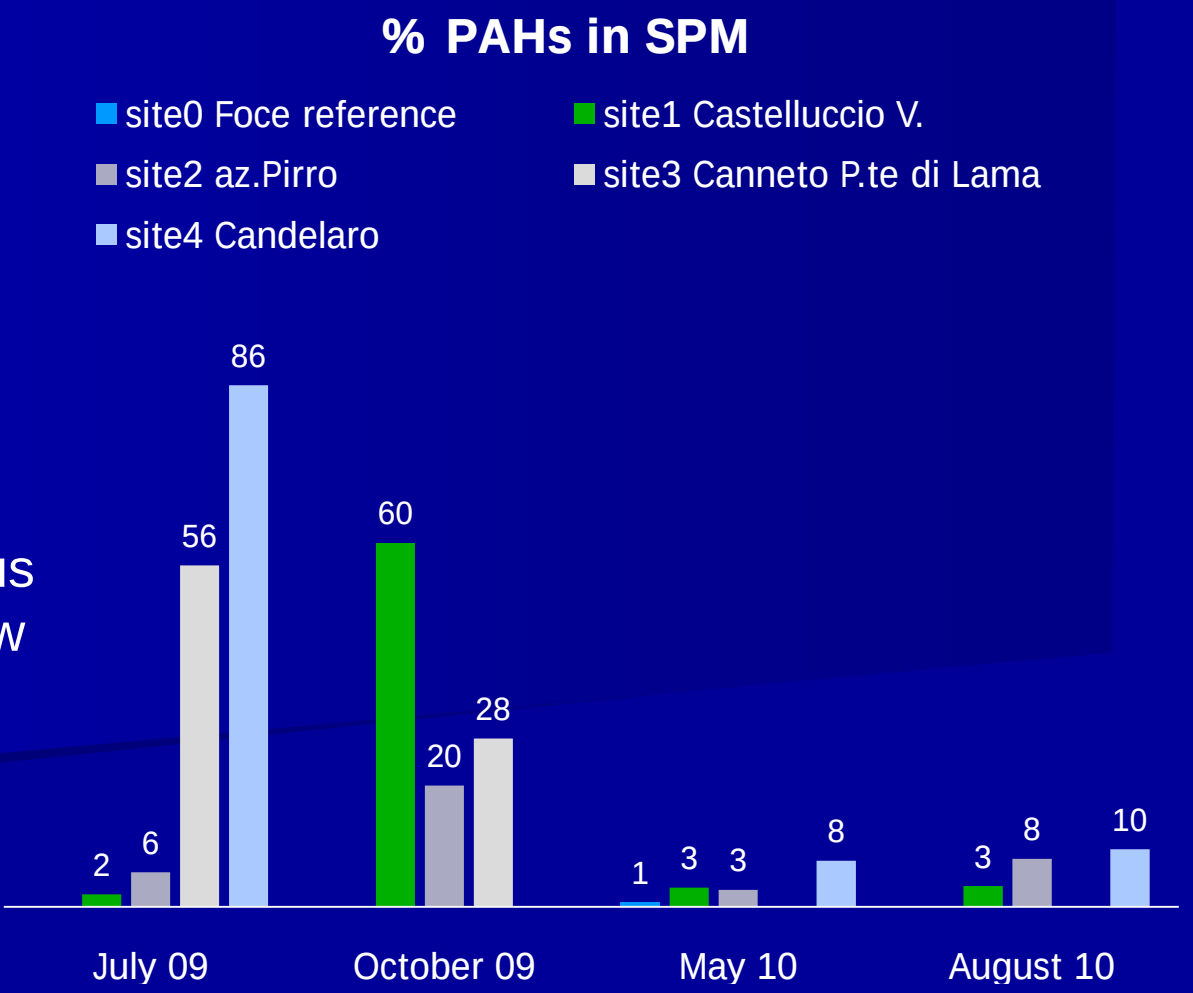
No clear trend for different congeners: loss is not correlated with volatility

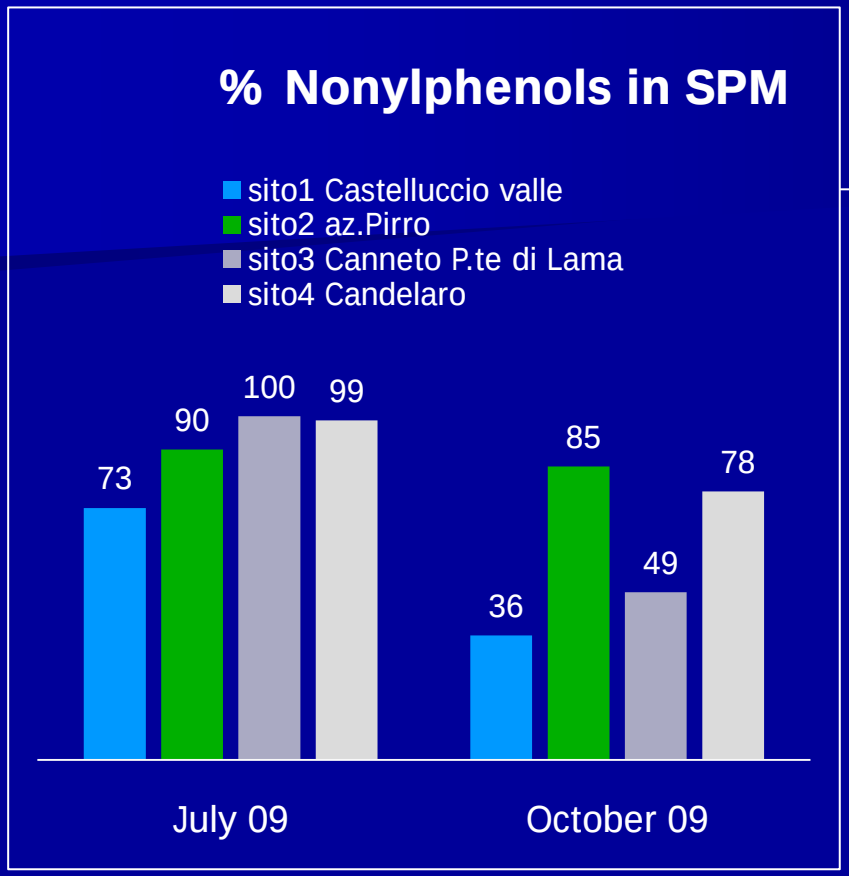
Solid transport during a high flow event (July 2009)



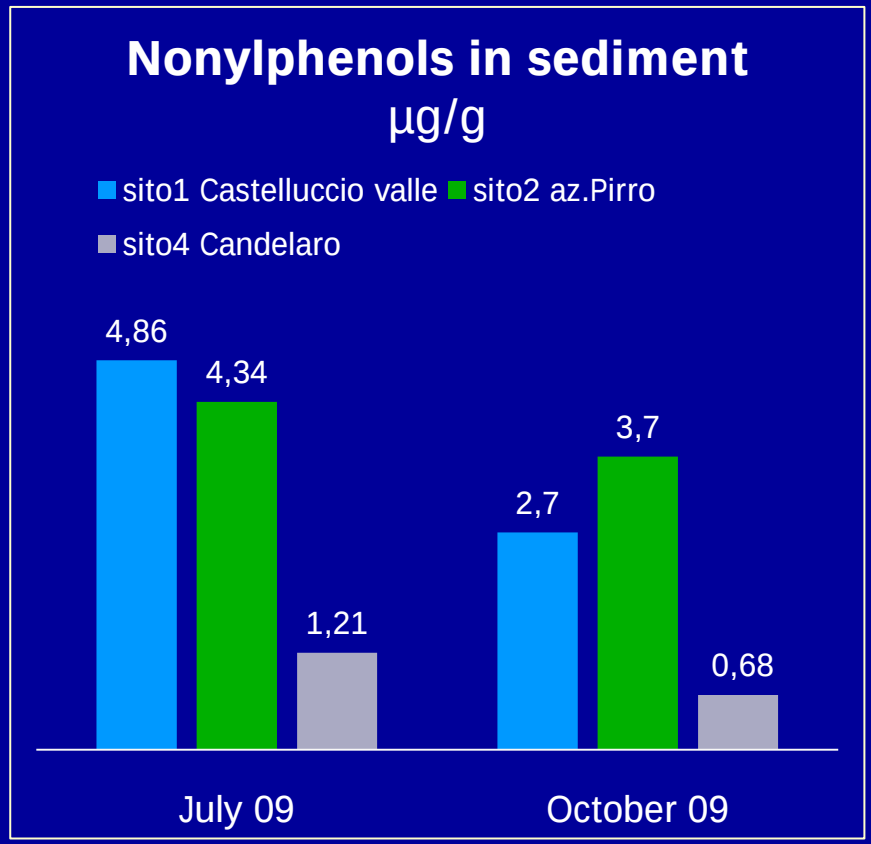
% of PAH adsorbed on SPM respect to whole water concentration

Solid transport of hazardous substances during high flow conditions





Final sink in sediment



Fate of organic substances in Celone basin: conclusions

- There are differences in the deposition and accumulation of organic substances in depositional (pool) and running (riffle) areas which depends on the substance sources and physico-chemical characteristics
- Generally in dry sediment there is a loss in concentrations respect to wetted sediments.
- The mechanism of this reduction is not understood (photodegradation?) but we can exclude volatilisation for PAHs
- During peak in flowrate with high solid transport, the run off from the basin and the resuspension from bed sediment increase solid transport of organic substances

Conclusions

- Assessing the risk of hazardous substances in temporary rivers requires the knowledge of the hydrological regime
  - A dry period reduces concentrations in sediment of organic substances
  - A flood event increases concentrations and transport of hazardous substances
- Different ecological habitats (pools and riffles) can be subjected to different toxic pressures
- Monitoring plans should take into account the peculiarities of temporary rivers. Suggestions:
  - Increasing of sampling frequencies in summer season to follow the hydrological regime
  - Sampling of SPM during discharge peak.
  - Sampling different hydrological features to support ecological quality assessment


Thanks you
for your
attention!