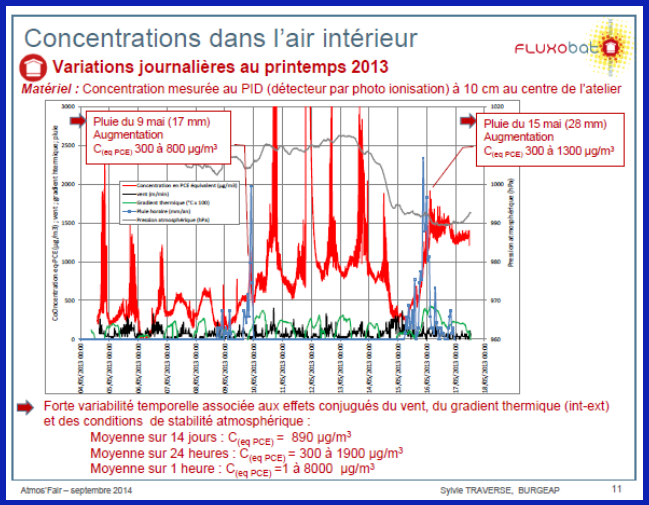
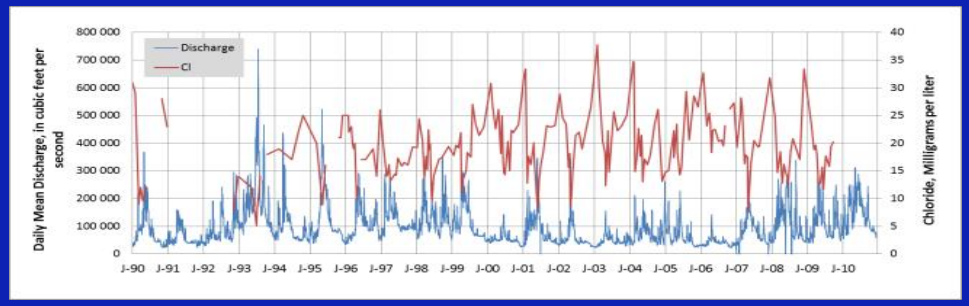
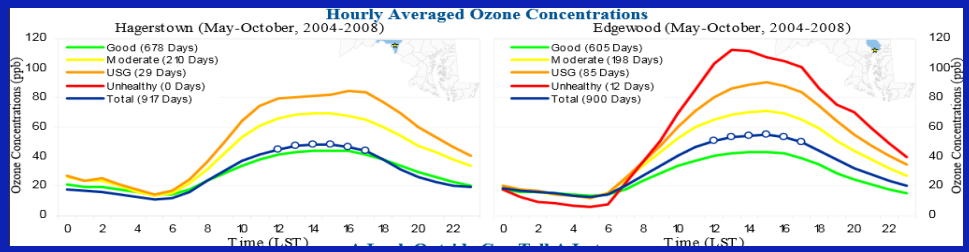
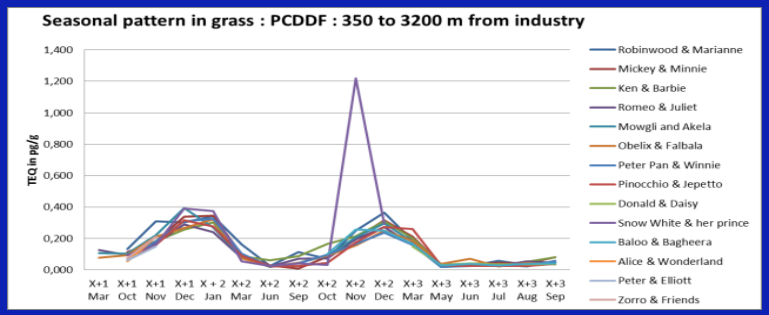
Temporal cycles in pollutants concentrations









Chris Balouet, PhD, Environment International
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Balouet.jean-christophe@neuf.fr
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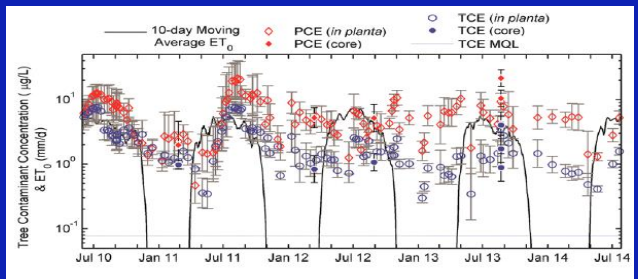


Conference Intersol March 2015 ;

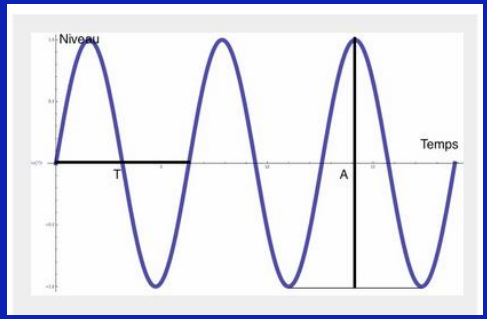
Daily and annual cycles in pollutants' concentrations…

Such temporal cycles are best documented in atmopshere when are also to be found in other environment compartments : pedosphere, lithosphere, hydrosphere, biosphere.

Such temporal cycles can be directly correlated to cycles in pollutant emissions. They can alternatively be caused by physical, chemical, biological, or meteorological factors.

They are documented for most of the pollutant families.

They are characterized by their period (i. e :day, year),
And their amplitude (up to 4 times fold not uncommon)



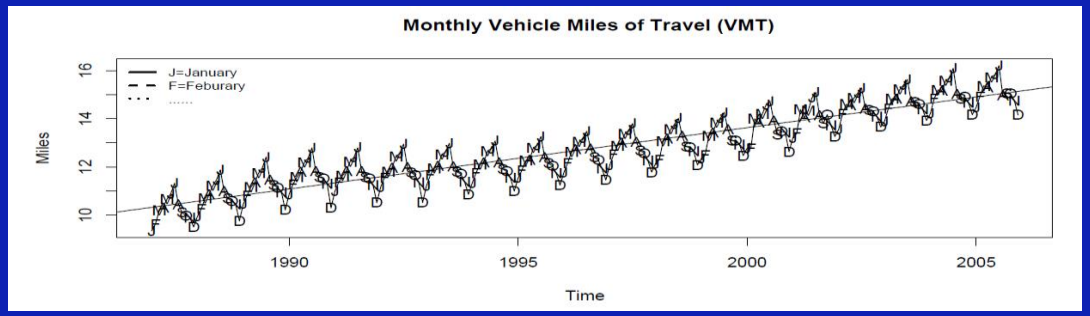
Drivers to Temporal concentration cycles

Anthropic versus natural.

Anthropic : pollutant emission flow, human activity

Natural : physico-chemical, including T° (daily and annual cycles) and P, sun light (i. e. UV), precipitations, Biological

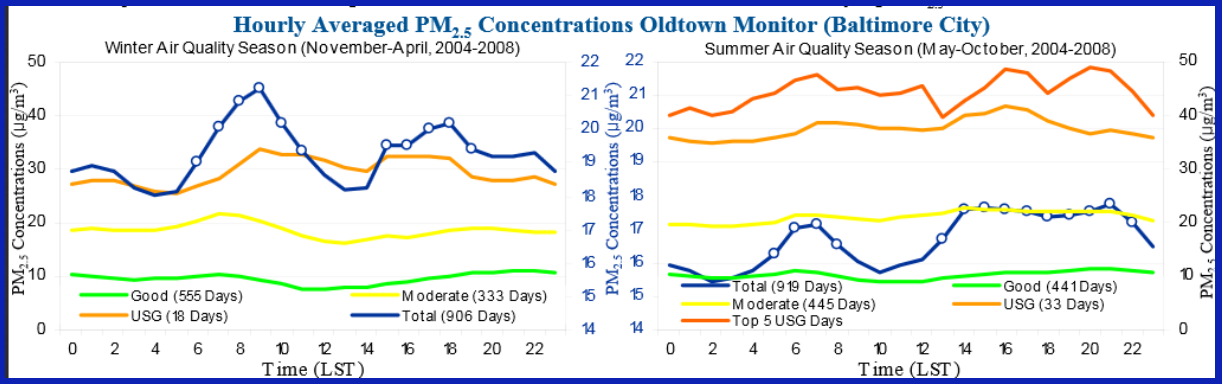
Some pollutants present daily + annual and eventually weekly concentration cycles ‘i.e. ozone, as a combination of multiple factors.



Now, let’s look at some atmospheric, surface water and biological concentration cycles

Temporal cycles = f pollutant emission In air

Daily cycles in atmospheric ozone and PM 2.5



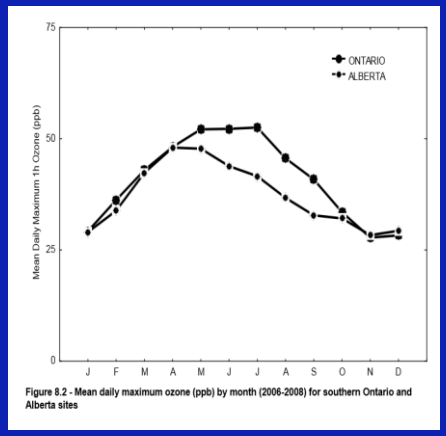
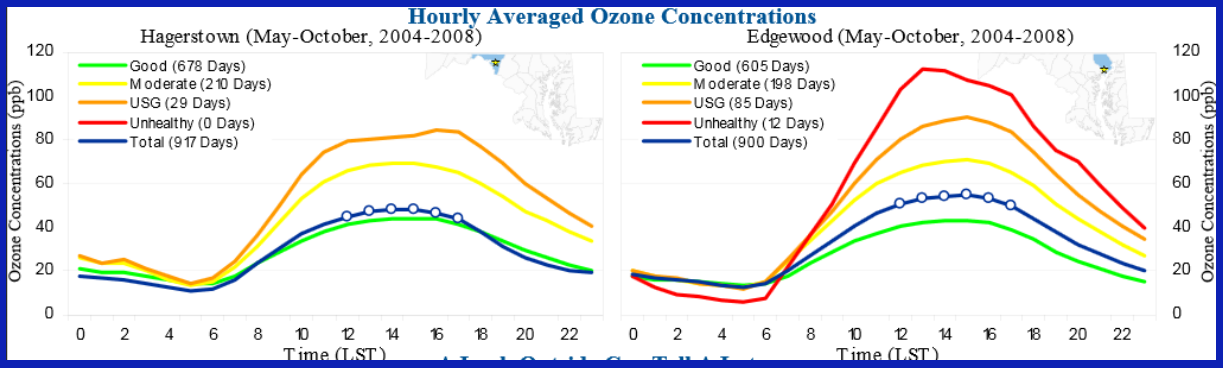


Figure 8.2 - Mean daily maximum ozone (ppb) by month (2006-2008) for southern Ontario and Alberta sites



Note that PM has two daily peaks (vehicle trafic).

Temporal cycles in air

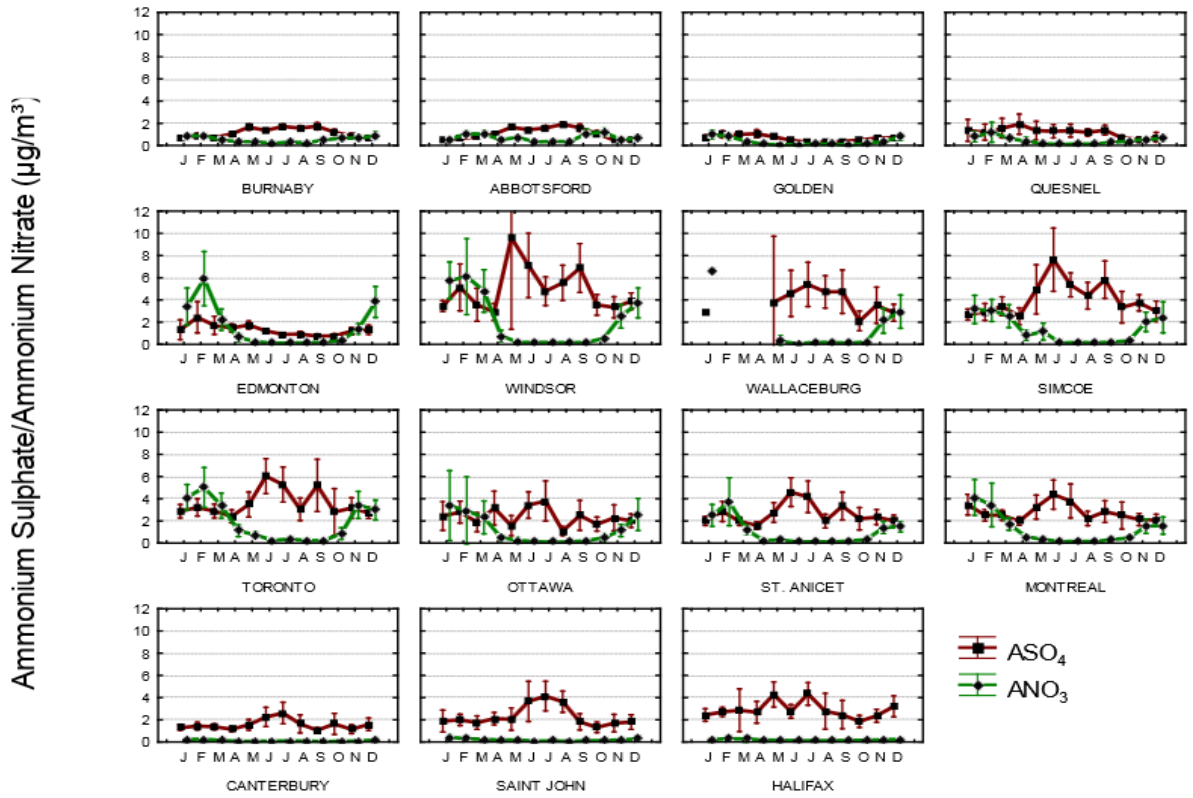
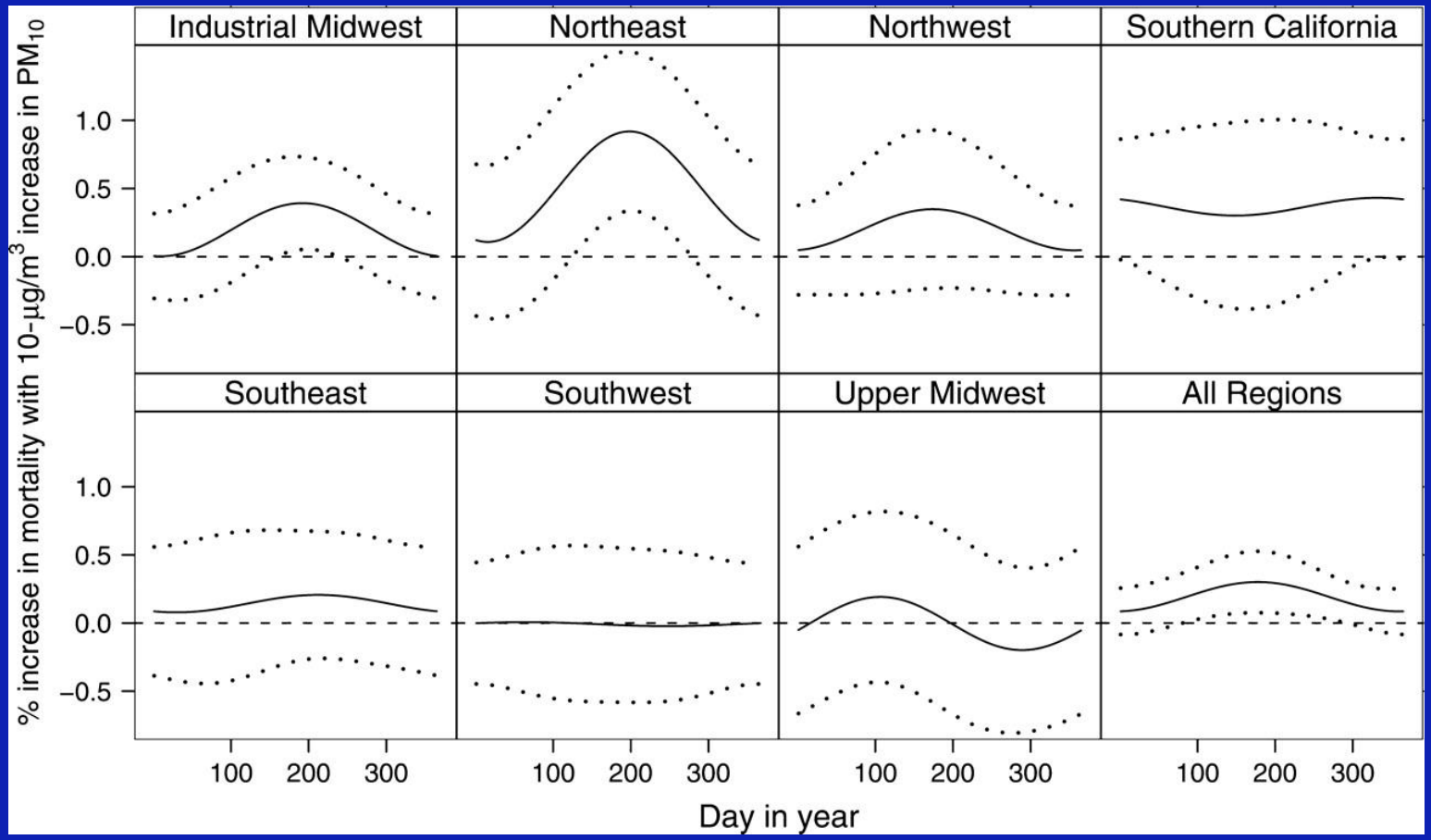


Figure 9.5 - Comparison of ammonium sulphate and ammonium nitrate concentrations (µg/m³) by site and month for years 2005 to 2008

Monthly means and the 90th percent confidence interval around the mean are plotted.

Annual concentration profiles for ammonium sulfate and ammonium nitrate. Note that these cycles are opposed during summer months.

EPIDEMIOLOGY : National and regional smooth seasonal effects of particulate matter less than 10 μm in aerodynamic diameter (PM10) at a lag of 1 day for 100 US cities, National Morbidity and Mortality Air Pollution Study, 1987–2000.

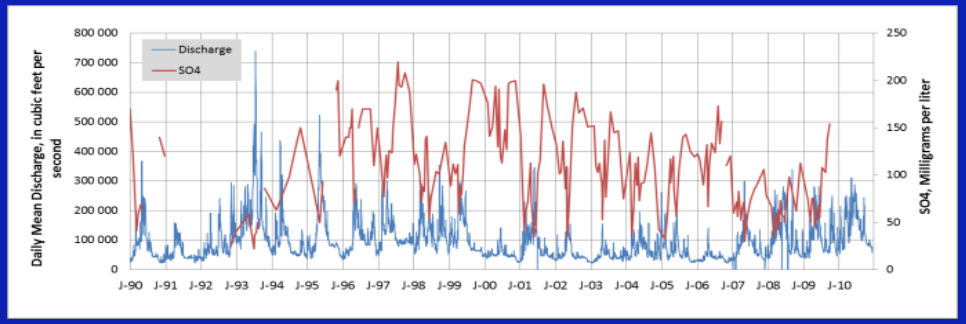


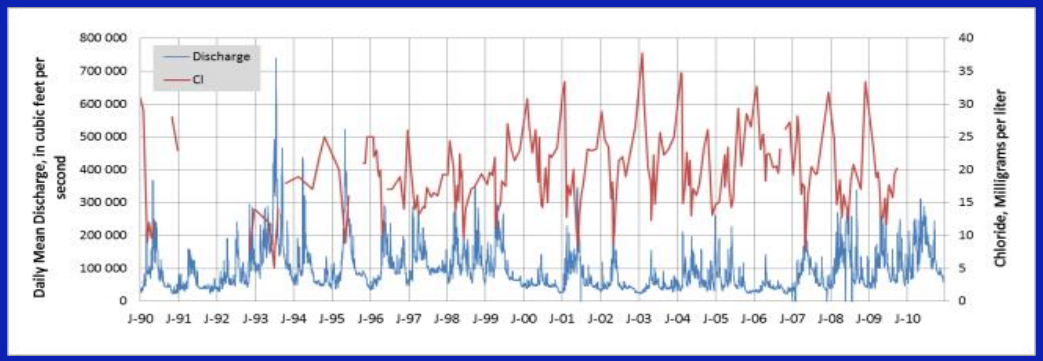
Peng R D et al. Am. J. Epidemiol. 2005;161:585-594

American Journal of EPIDEMIOLOGY

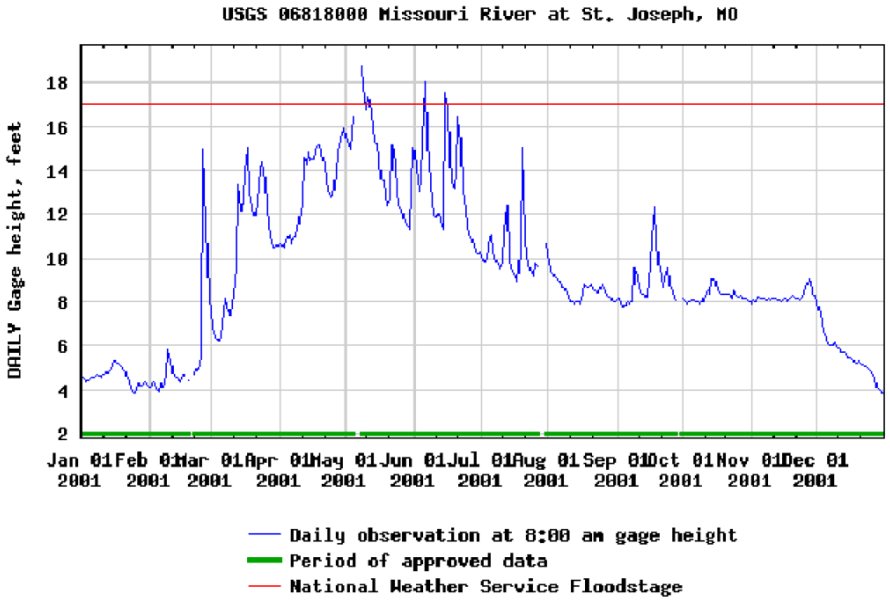
Annual cycles in surface water

Cl^- and $SO4^{--}$concentrations in Missouri river, as measured between 1990 and 2010 (J for January), basically every two weeks, by the US Army Corpse of Engineers. The higher the river flow (spring), the lowest concentrations are found ; concentrations are at their highest in January, varying within the year by an average 3 time fold.





High river stages influence nearby GW



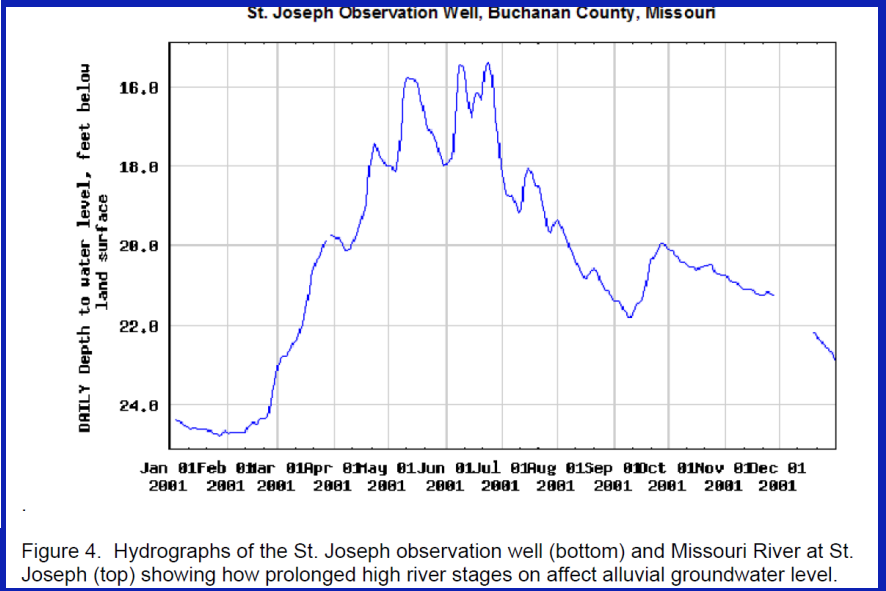


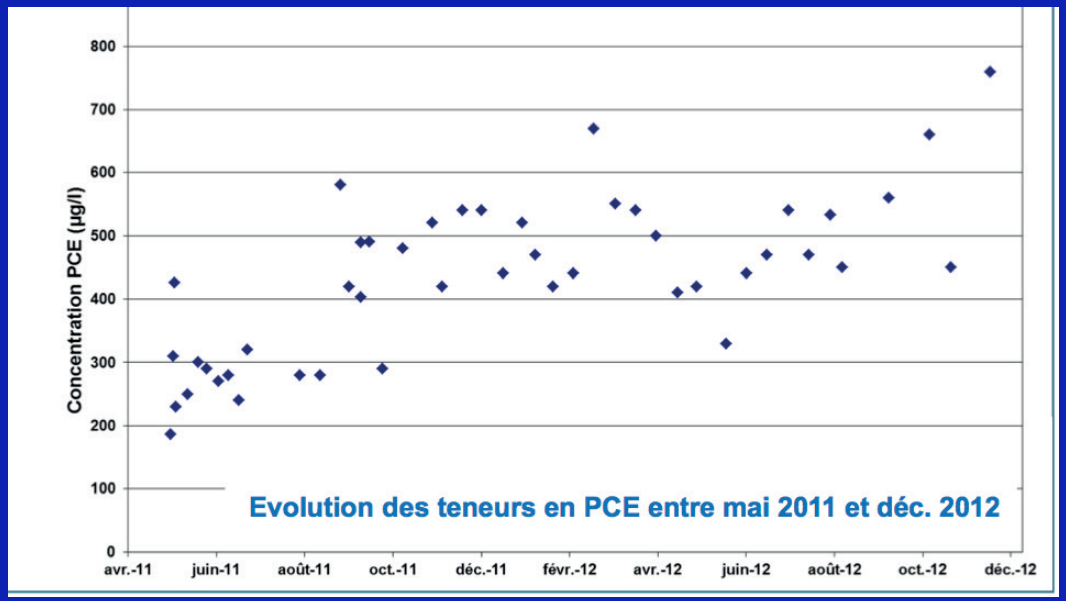
Figure 4. Hydrographs of the St. Joseph observation well (bottom) and Missouri River at St. Joseph (top) showing how prolonged high river stages on affect alluvial groundwater level.

So do precipitations…

Oceanic tides also influence GW level in tidal zones.

We will see later the combined effects of precipitations, changes in T°, barometric pressure on indoor air's pollutant concentrations

Annual cycles in GW



Evolution of GW PCE concentrations from a potable well (Ayroule / Foix). www.ades.eaufrance.fr

Note the high PCE concentrations from september to march and the doubling of concentrations between summer and winter.

Such kind of data is kind of scarce.
Your help is most welcome to get more.

Several parameters can influence contaminant concentrations, including precipitations, T°, biological activity… when other mechanisms are affecting groundwater, and illustrated below. The influence of these parameters in the hereby cases should indeed be further investigated…

Table 1. Concentrations of cVOCs (mg/L) in Groundwater Monitoring Well Nearest Measured Trees

date	PCE	TCE	cDCE
4/23/2009	0.230	0.039	0.021
9/22/2009	0.175	0.029	0.018
3/30/2010	0.283	0.048	0.027
8/16/2010	0.554	0.058	0.050
12/02/2010	0.955	0.067	0.043
5/4/2011	0.680	0.158	0.177
8/15/2011	0.573	0.129	0.143

Another case published by Limmer et al., 2014…

Some natural factors affecting groundwater depth

To and fro movements of watertable due to solar /lunar tides, barometric pressure changes, precipitations or pumping, which contribute to :

- pollutant dispersion & spreading.
- up and down movements of floating contaminants.
- modifying groundwater's capillar fringe.
- expulsing gaseous contaminants (precipitations, tides, barometric pressure).

  Precipitations are commonly associated to barometric pressure changes. Night and day barometric cycles combine their sinusoidal effects with groundwater tides.

Pumping and precipitation

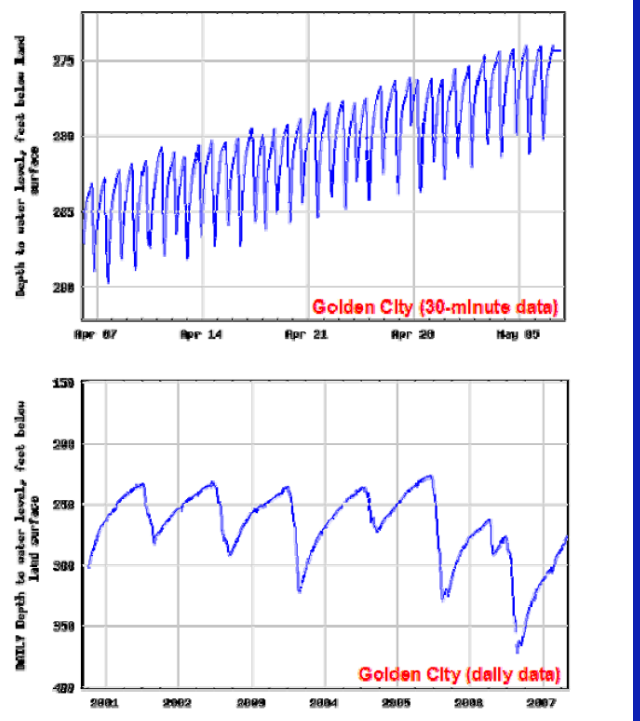


Figure 7. Daily water-level fluctuations due to nearby municipal pumping (top) and seasonal drawdown and recovery patterns resulting from extensive local irrigation (bottom) at Golden City

Pumping water from GW wells (above left) causes lowering of water table, when annual cycles are clearly influenced by precipitations as for recharge.

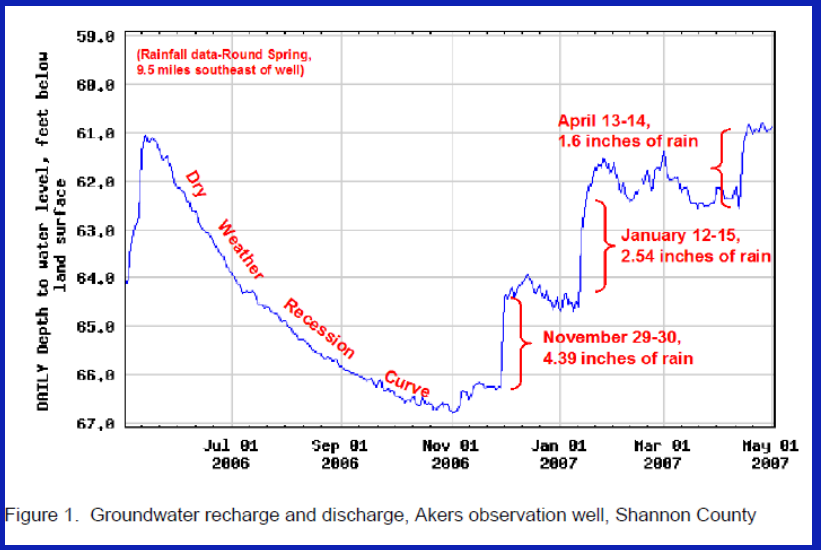


Figure 1. Groundwater recharge and discharge, Akers observation well, Shannon County

Groundwater tides

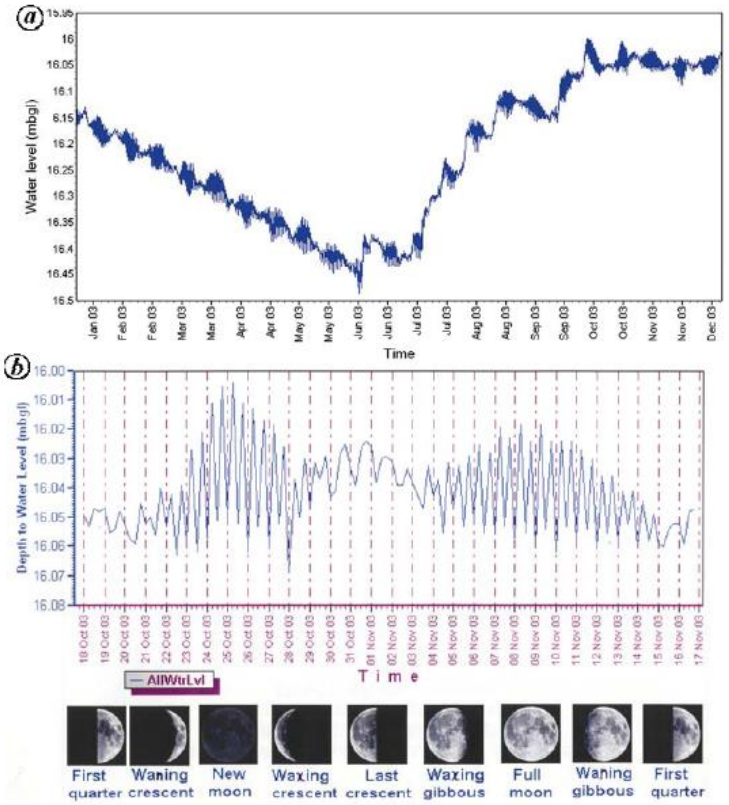


Figure 6. *a*, Hydrograph recorded at Kothagudem (2003), Khammam District, Andhra Pradesh, India. *b*, Hydrograph recorded and comparison of piezometric head with different phases of Moon at Kothagudem.

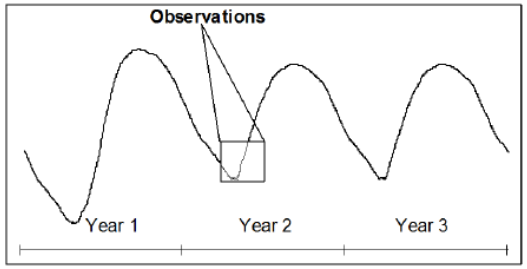


Figure 3: Schematic diagram showing time-evolution of groundwater level in a monsoon region

Diurnal cycles are influenced by sun, T°, and moon cycles (2 per day).
These cycles are also influenced by altitude, latitude

Establishment of earth tides effect on water level fluctuations in an unconfined hard rock aquifer using spectral analysis
JC. Maréchal1, M.P. Sarma2, S. Ahmed3 and P. Lachassagne4

Barometric pressure

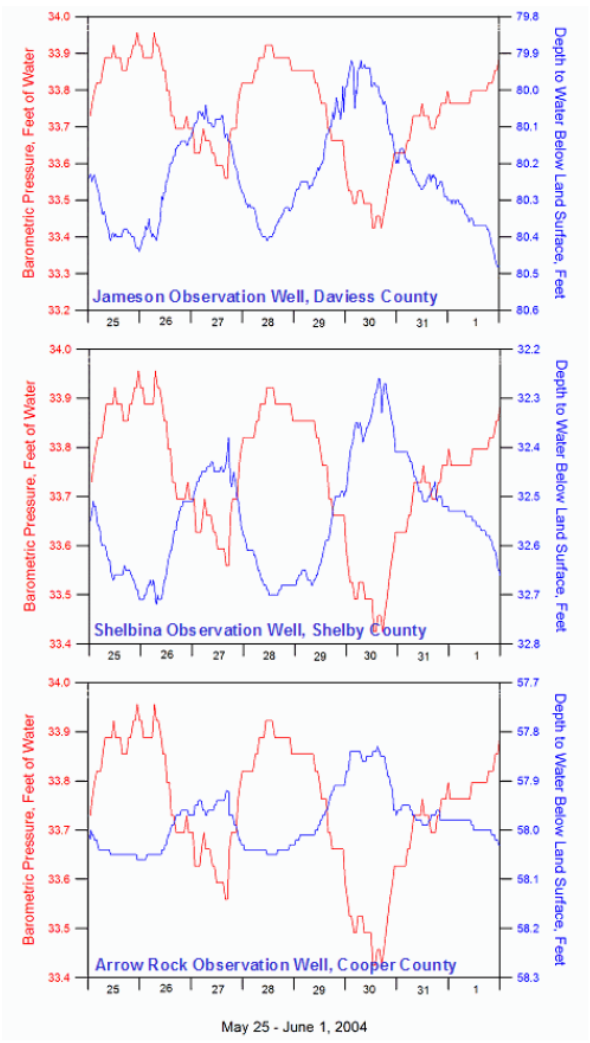


Figure 9. Hydrographs of Jameson, Shelbina, and Arrow Rock observation wells (blue) and barometric pressure at Sanborn Field, University of Missouri-Columbia (red) showing the effects of barometric pressure changes on groundwater levels.

Aquifer level changes by 19 cm for 0,6 inches Hg.
Barometric Efficiency (BÉ) as a function of porosity.

Mind measure at well head's level.
Electronic systems corrected for barometric changes.
Immediate response (increase in barometric pushing watertable down. Lag before equilibrium by several hours).

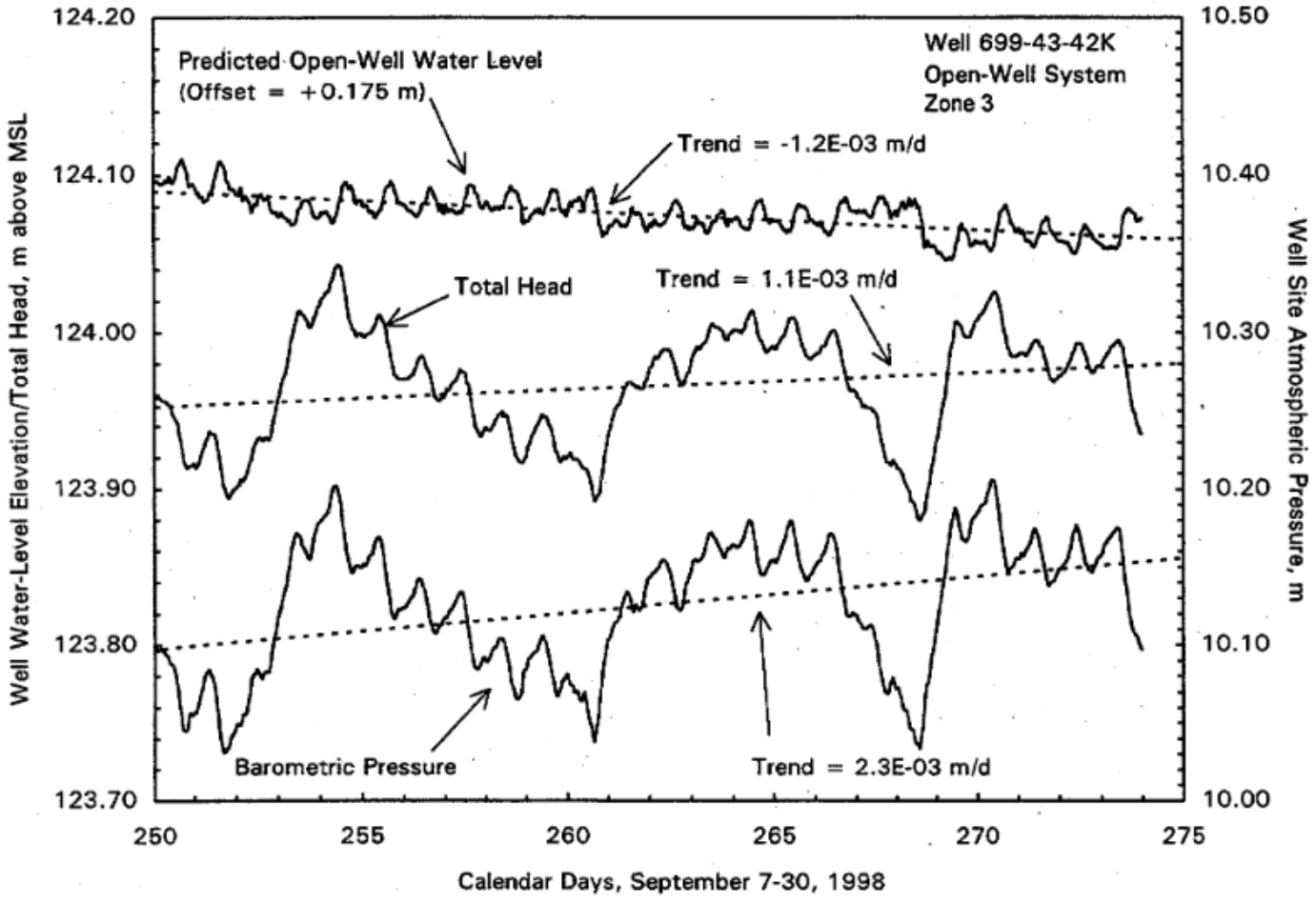


Figure 4.4. Total Head and Atmospheric Pressure Measurements for Well 699-43-42K Zone 3 (open-well system), September 7 - 30, 1998

http://www.osti.gov/scitech/servlets/purl/15125

Some lag time…

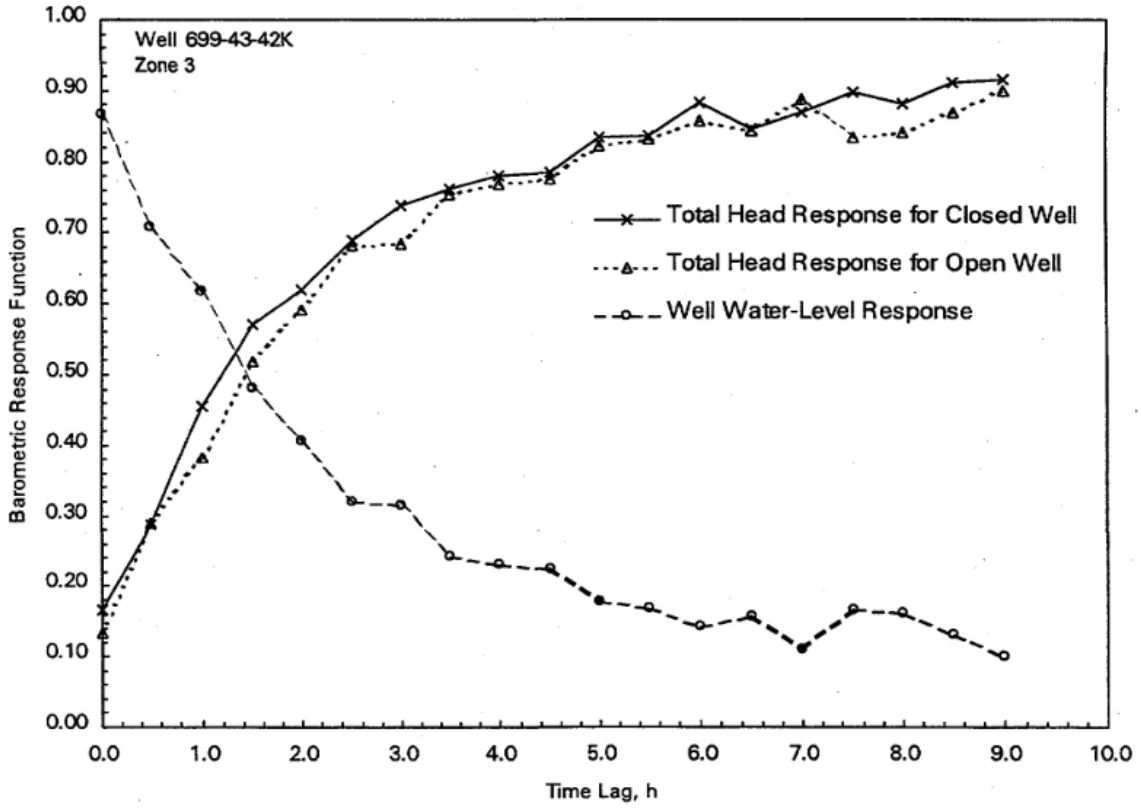


Figure 4.5. Comparison of Open Versus Closed System Total Head Barometric Response Patterns for Zone 3

EarthQuakes

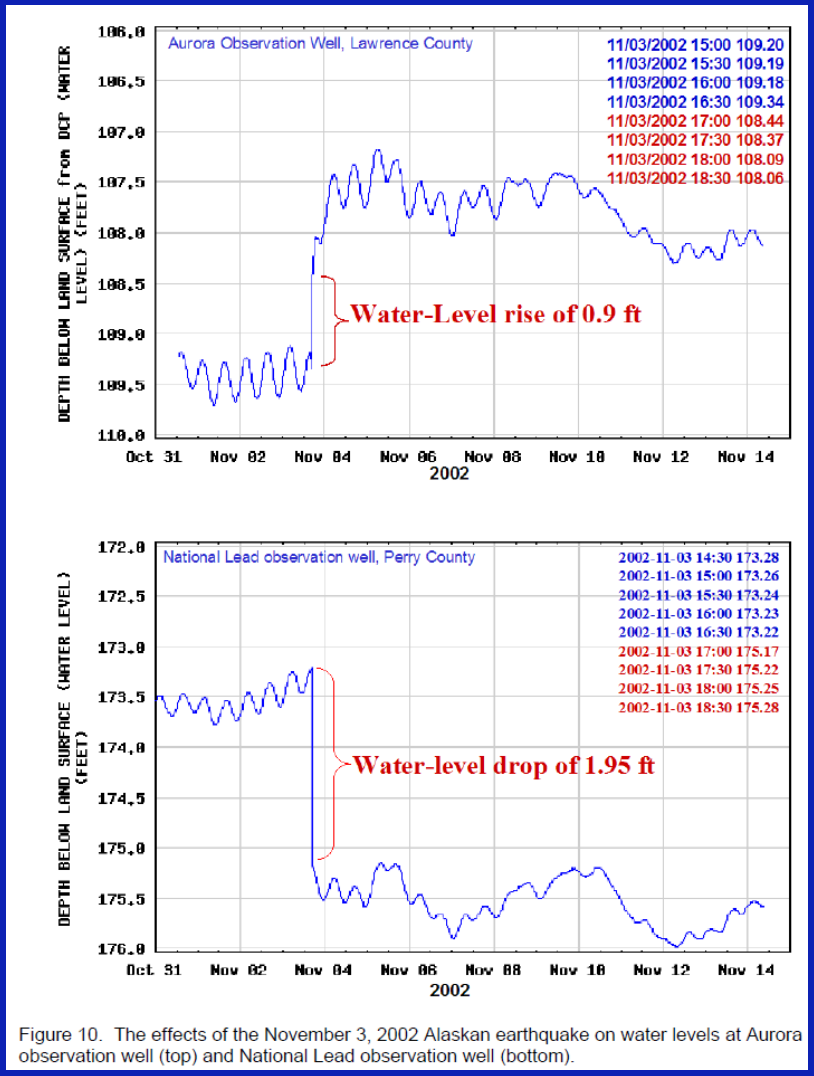


Figure 10. The effects of the November 3, 2002 Alaskan earthquake on water levels at Aurora observation well (top) and National Lead observation well (bottom).

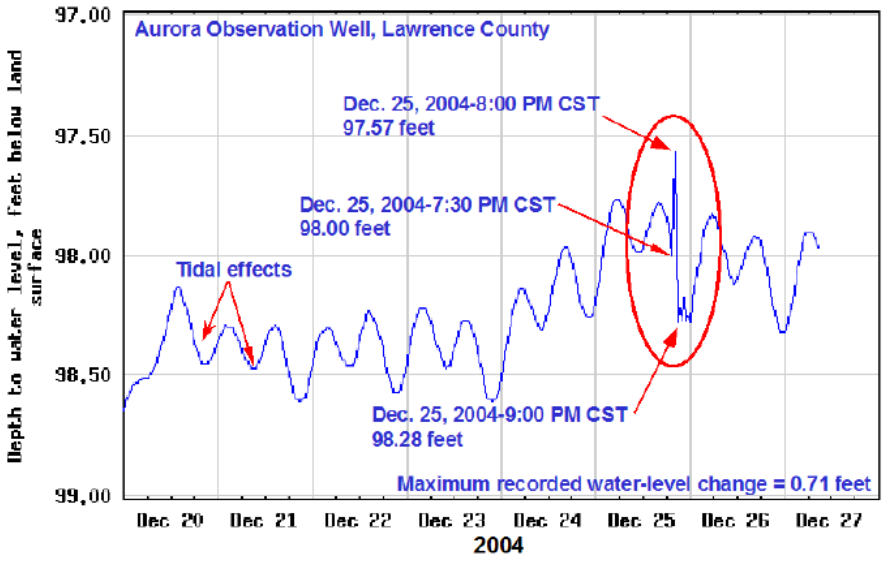


Figure 11. The effects of the December 2004 Sumatra earthquake on water level at the Aurora observation well.

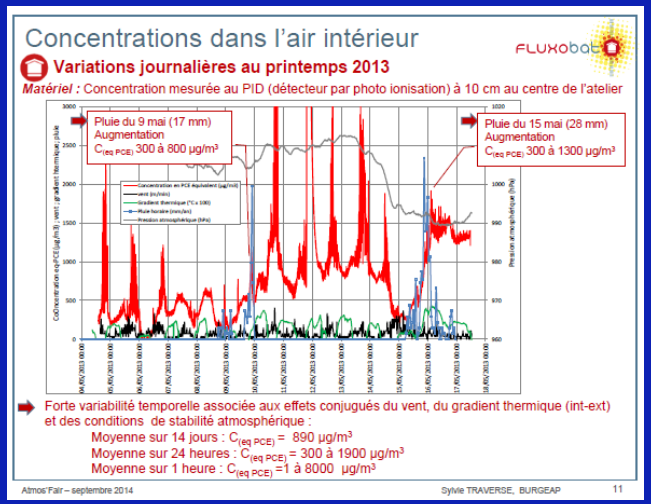
Tide cycles changing land aquifer depth by 15 cm in amplitude

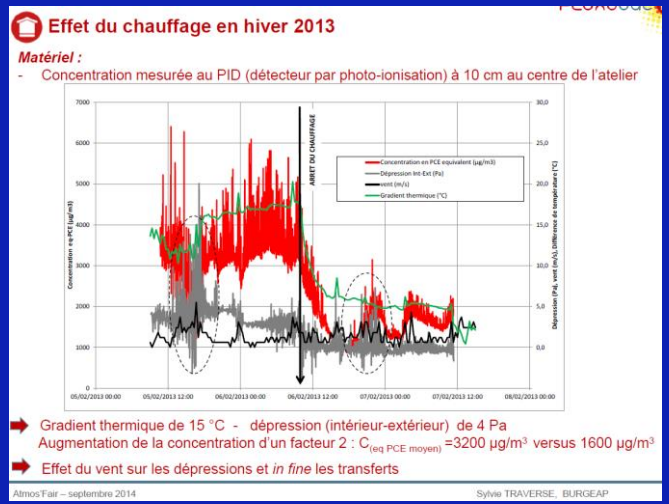
Remote earthquakes causing up to 60 cm change in land aquifer depth.

Complex / multifactorial cycles : indoor air

investigations conducted inside a building, located by a PCE plume, clearly demonstrated daily cycles with a minimum 3 time fold amplitude, as well as enabled to document the role of precipitations : the more rain, the higher daily averages.

Further investigating this case, the role of heating and outdoor winds, causing a higher depression between indoor and outdoor, proved to cause increased indoor air PCE concentrations.





Some mechanisms?

Physical : Temperature modifying solubility, henry's constant for evaporation, increasing biological activity.

Day light causing photolysis,

Meteorological : Precipitations dissolving pollutants during lixiviation, washing surficial soils, accumulating on top of water table. Pushing soil gases upwards.

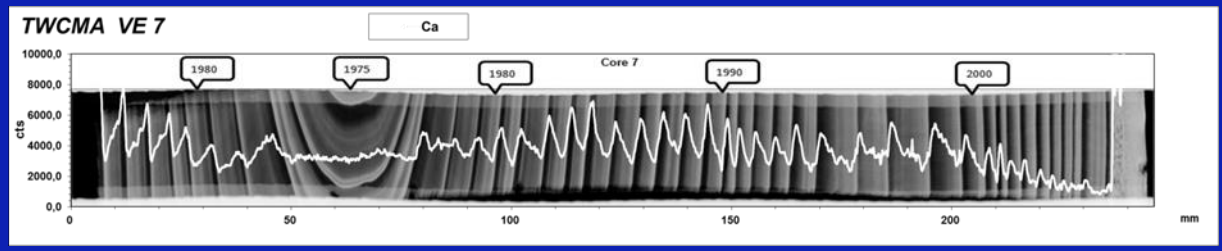
Winds diluting atmospheric contaminants.

Biological : plants growth, foliage cycles.

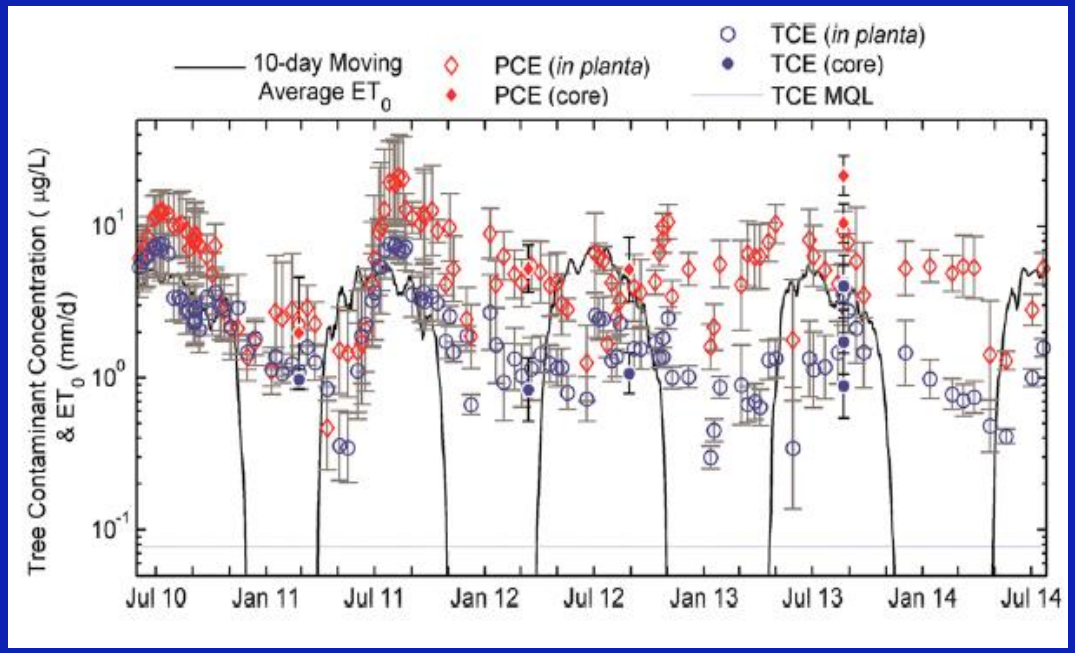
Many have been determined as having both daily and annual periods (i.e. ozone, PM,

Annual cycles in plants

Natural cycle for Ca in annual rings.

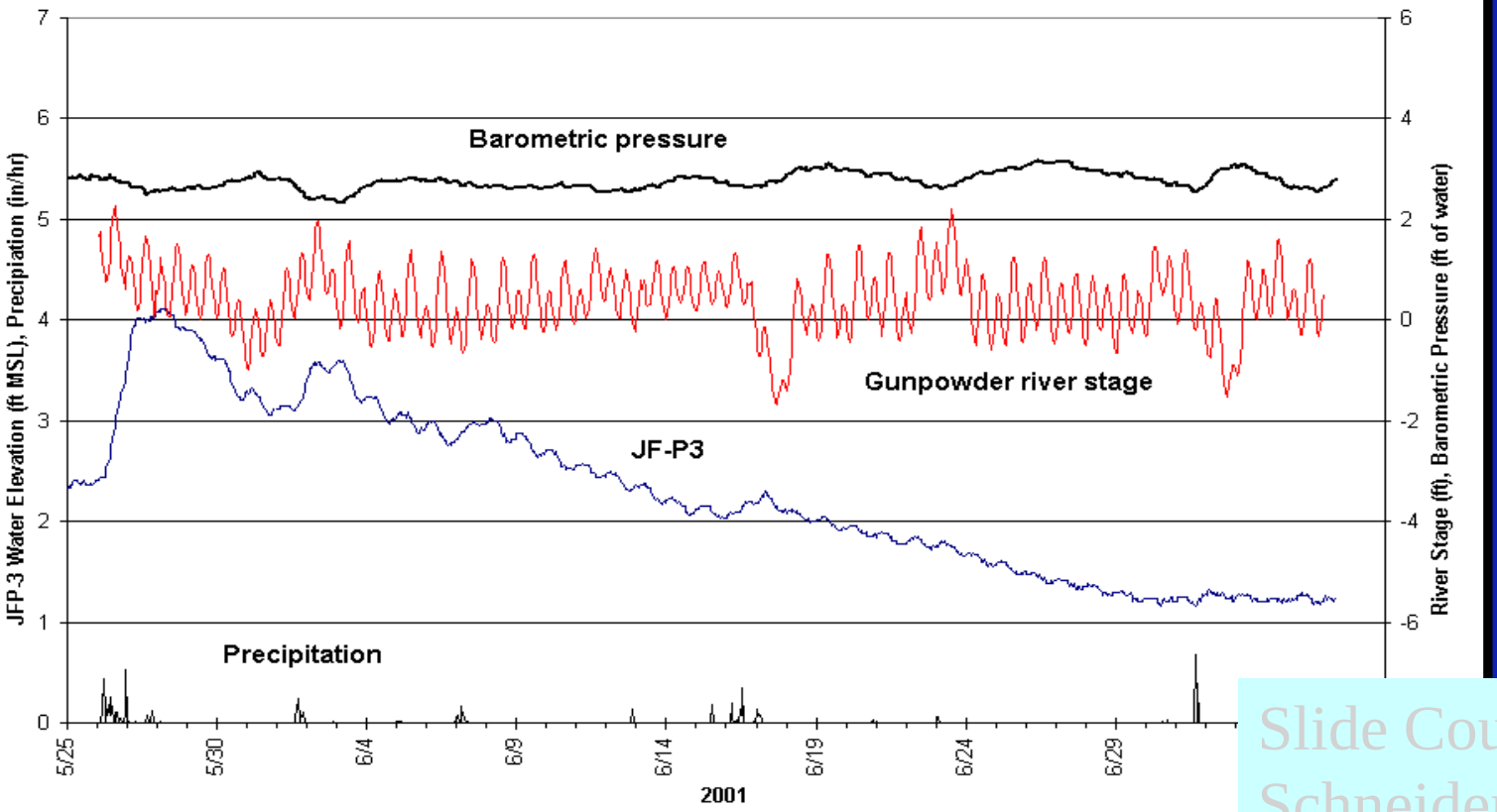


Elemental concentrations in wood tissues are higher in spring, similar to what is found in surface water. However, pollutant concentrations in trees sap are higher in summer, as documented here for PCE and TCE.



Annual and daily cycles by plants

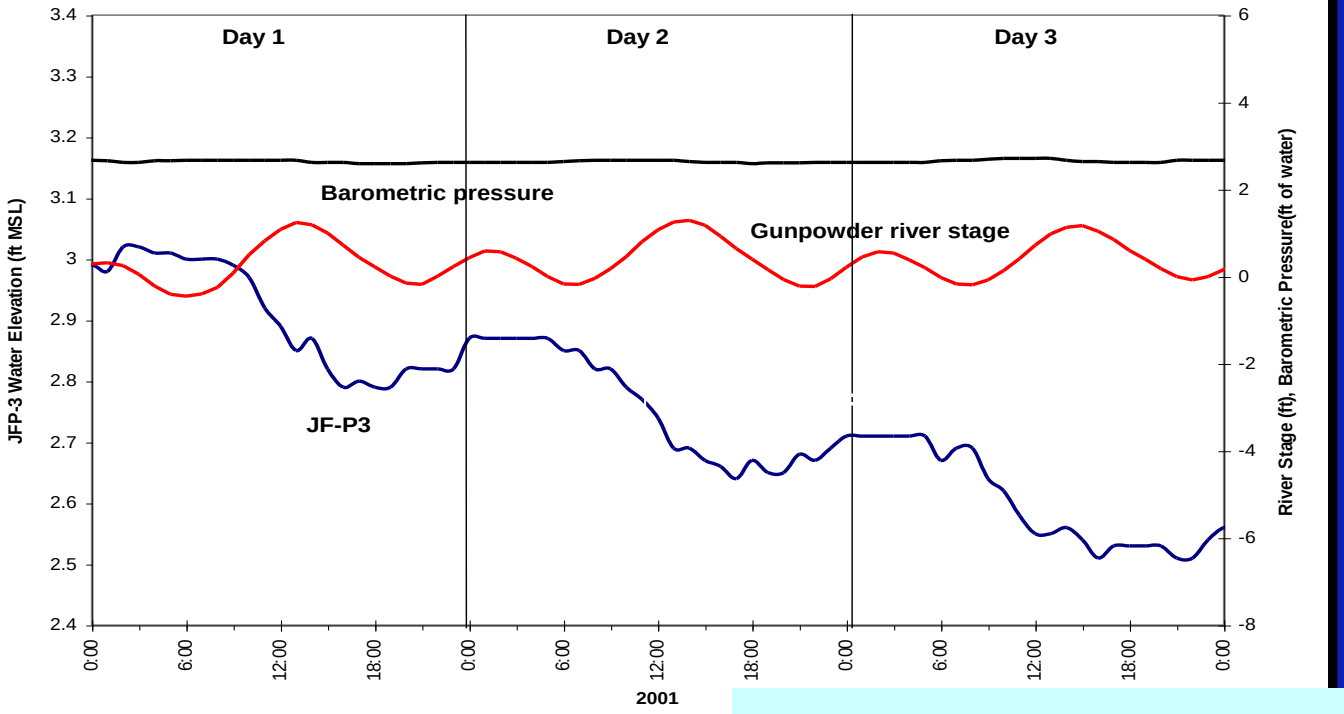
Diurnal cycling of energy driven by evapotranspiration can cause considerable fluctuations in groundwater, ‘removing water during the day an the groundwater potential can ‘recover’ at night.



Slide Courtesy of Bill Schneider, Weston

Annual and daily cycles by plants

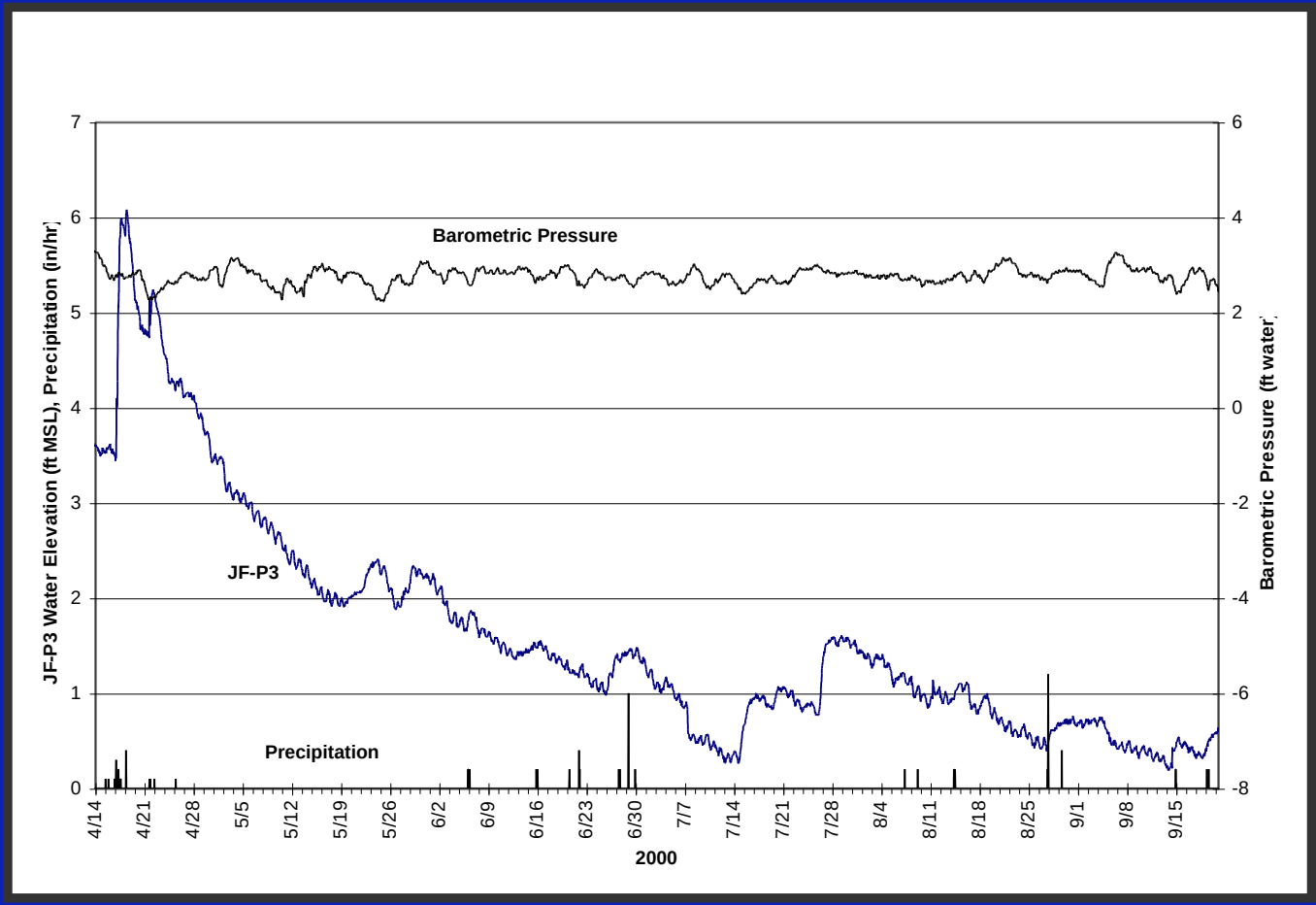
Diurnal cycling of energy driven by evapotranspiration shown on a daily basis. Each drop is linked to the climate, as sunlight, wind and temperature drive the ET by the overlying trees. Fluctuations at this coastal site in Maryland US are independant of tidal fluctuations.



Slide Courtesy of Bill Schneider, Weston

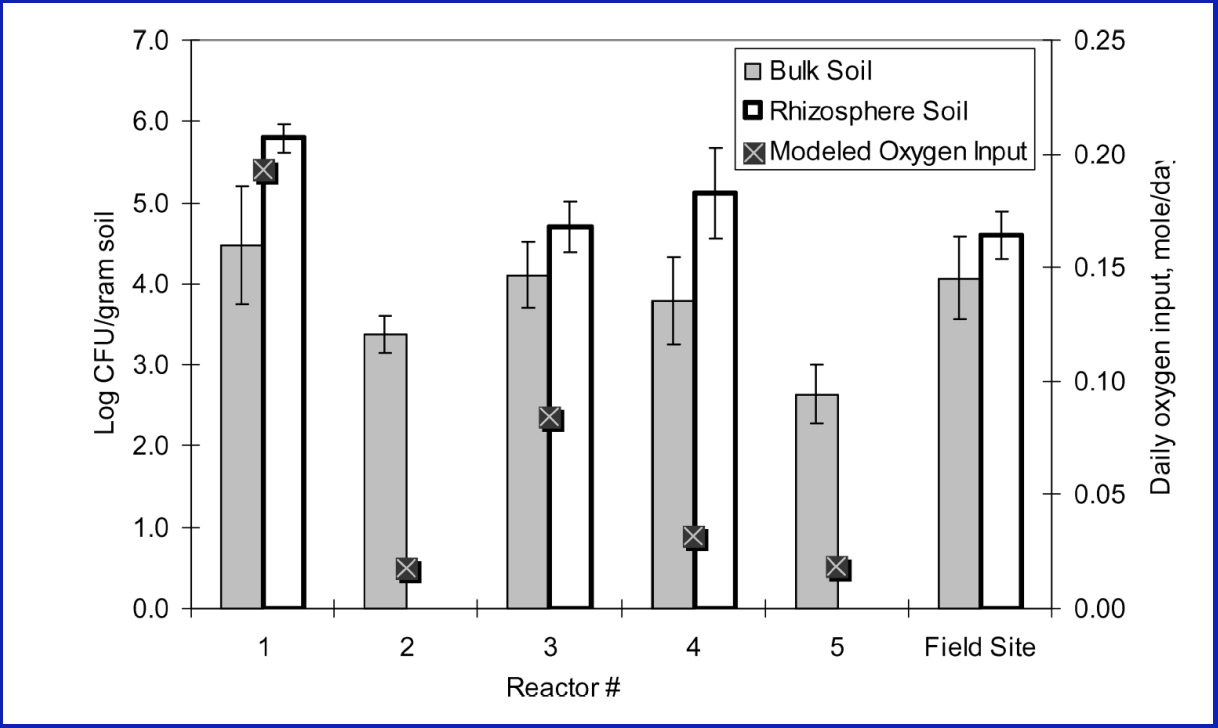
Annual and daily cycles by plants

The seasonal draw down and the diurnal daily impacts of plants can greatly enhance the oxygen transport into the subsurface and pollutant transport from deeper groundwater.



Annual and daily cycles by plants

Diurnal cycling of energy driven by evapotranspiration can cause transfer of oxygen to fuel biodegradation, In stis study Reactor 1 was planted, and exposed to BTEX, increasing both oxygen transfer and BTEX degrader populations.



Weishaar, J.A., D.T. Tsao, and J.G. Burken (2009) *Int. Journal of Phytoremediation*. 11(5); 509 - 523

Annual and daily cycles by plants

In a related study the degree of diurnal cycling was controlled, revealing that the combined groundwater drop (seasonal impact) and diurnal cycling resulted in the greatest BTEX biodegradation

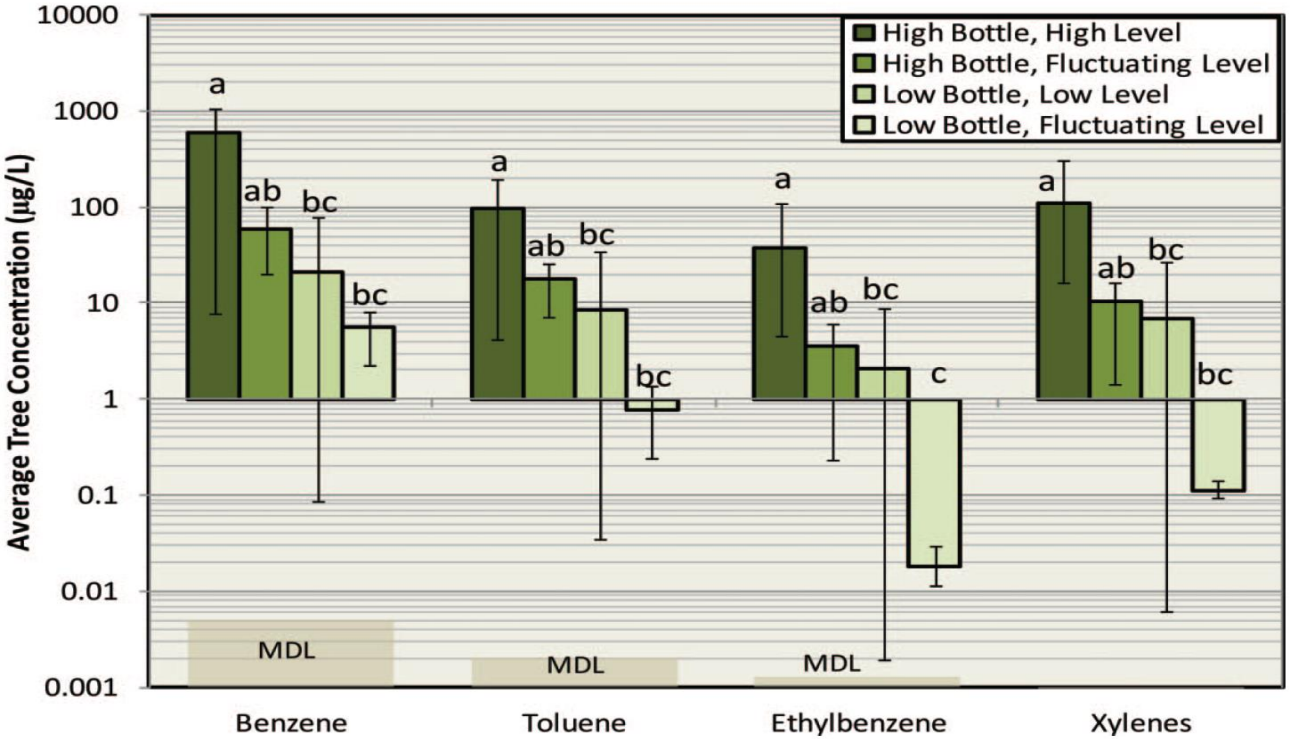
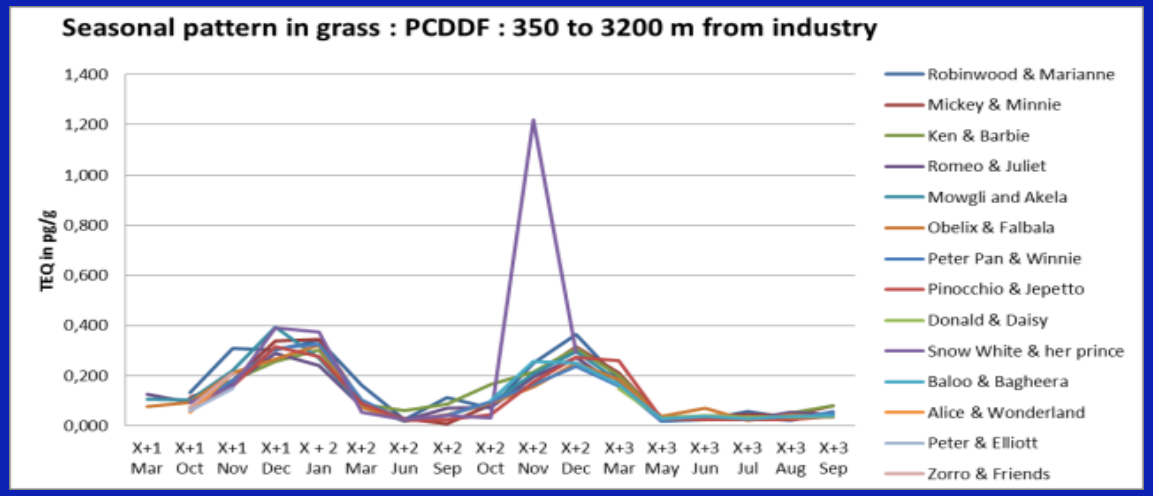


Figure 4 Average tree concentrations observed (error bars denote max and min) for dosing high concentration (same letters are not significantly different at 0.05 level) (color figure available online).

1. Wilson, J., Bartz, R.., Limmer, M.A., Burken, J.G. (2013) *International Journal of Phytoremediation*, 15 (9), 900-910

Annual cycles in plants

Alternatively, other seasonal cycles have been documented in grass, such as below, for dioxins and furanes. In this case, the winter enrichment in PCDF may be due to a combination of increased winter emissions by domestic heating, accumulation during plants dormant season, PCDF decrease in summer's plant concentrations due to grass growth, biodegradation, photolysis, increased evaporation at higher temperatures (Henry's constant).



Does it matter?

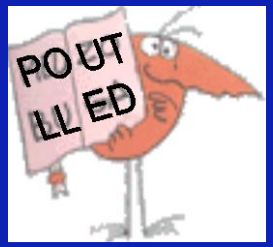
Documenting and understanding of these **multifactorial** cyclic phenomena is forensically essential.

i.e. when working with non continuous recording system, one or two parameter(s) only, or when to understand the very facts versus explain the whys of « abnormal » values from snapshot data.

Most solid documentation and research is further needed, on an international basis, for the same causes are expected to cause the very same effects worldwide.

Thank you for sharing further your concerns and positive data.

Conclusions



Environmental forensics
Is needed to understand & solve complex questions

« … It is factual evidence. Physical evidence cannot be wrong, it cannot perjure itself, it cannot be wholly absent.
Only human failure to find it, study and understand it, can diminish its value » Edmond Locard

Thank you.

Thank you

"The Truth, The Whole Truth, and Nothing But The Truth."

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And Joel Burken, Associate Professor,
Dept of Civil, Architectural and Environmental Engineering
University of Missouri-Rolla

Consecutive and asynchronous, versus cyclic releases?