



Cerema



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LMOPS

The benefits of Raman spectroscopy to monitor water quality near transportation infrastructures. From qualitative appreciation to the identification of organic pollutants traces

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Cerema Est

ICORS 2018, Jeju (Korea)
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Summary

Anthropogenic transportation activities and water quality

Specific case of airports

Ions related to urban configurations

Down to water courses

Conclusion

Anthropogenic transportation activities and water quality



spreading of NaCl roads
⇒ amounts 20-40 g/m²



degradation of vegetation along pavements
+
impacts on soils, rivers and ponds



pollution of rivers during and after
winter maintenance season



aircraft de-icing >50t (A319, A320, A330)
⇒ aspersion 160-650 L

Specific case of airports

Context and objectives

Increasing amounts of chemical products used on runways, taxiways and aircrafts

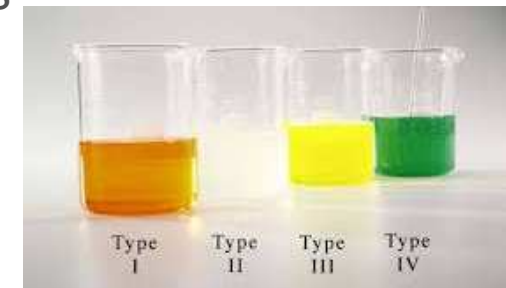
Absence of knowledge of residual amounts on treated surfaces
Economical and environmental concerns

Objectives

- to detect these chemicals (formates, acetates, glycols, fluorinated ethers ...),
- to discriminate the chemicals between each others,
- to quantify their amounts into water, included for large dilutions

⇒ **investigations on Raman spectroscopy**

anti-icing fluids



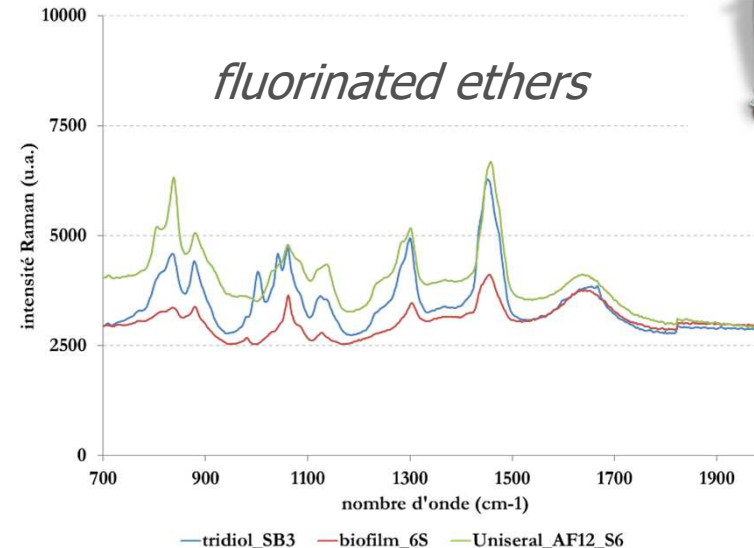
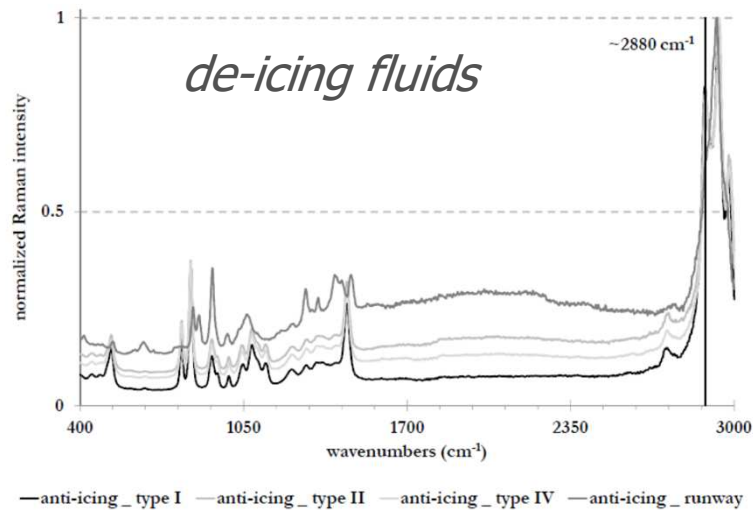
Specific case of airports

Raman data and analysis on airports fluids

Raman acquisition with aqueous solutions at different concentrations (from pure to 0.0004% v/v) in either de-icing fluids and fluorinated ethers

Measurements with Kaiser RXN-2, 785 nm, 150-3425 cm^{-1} spectral range

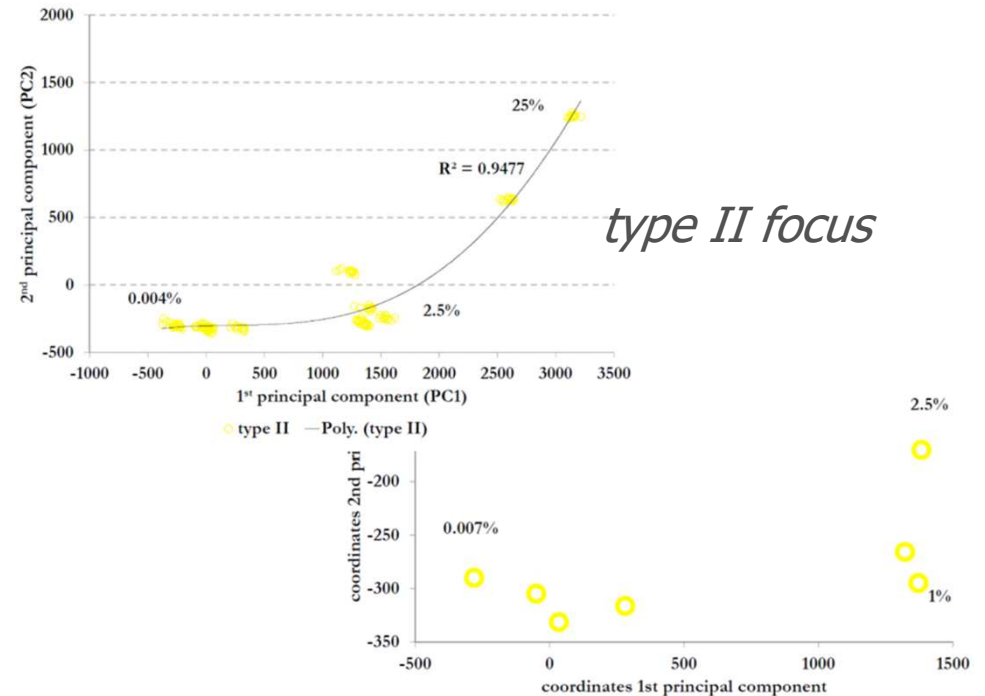
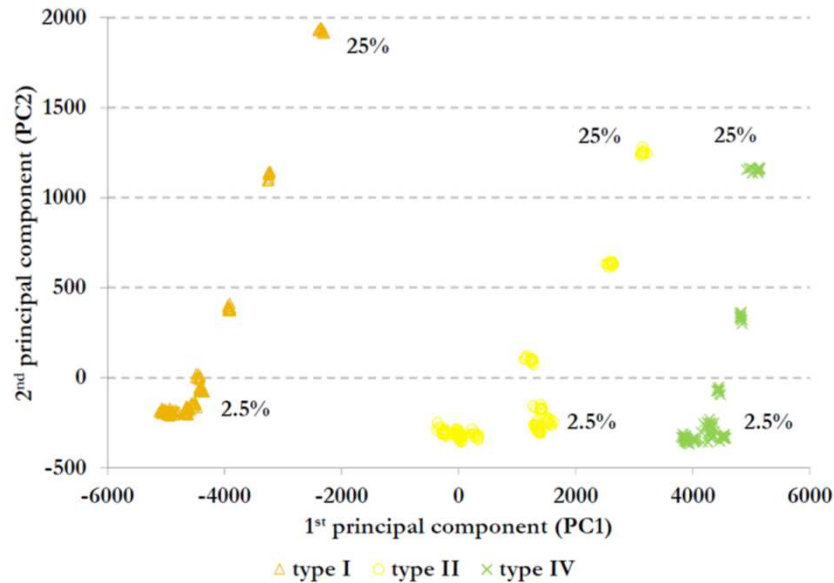
Integration time of a few seconds, with laser output of 100 mW maximum



Specific case of airports

Raman data and analysis on airports fluids

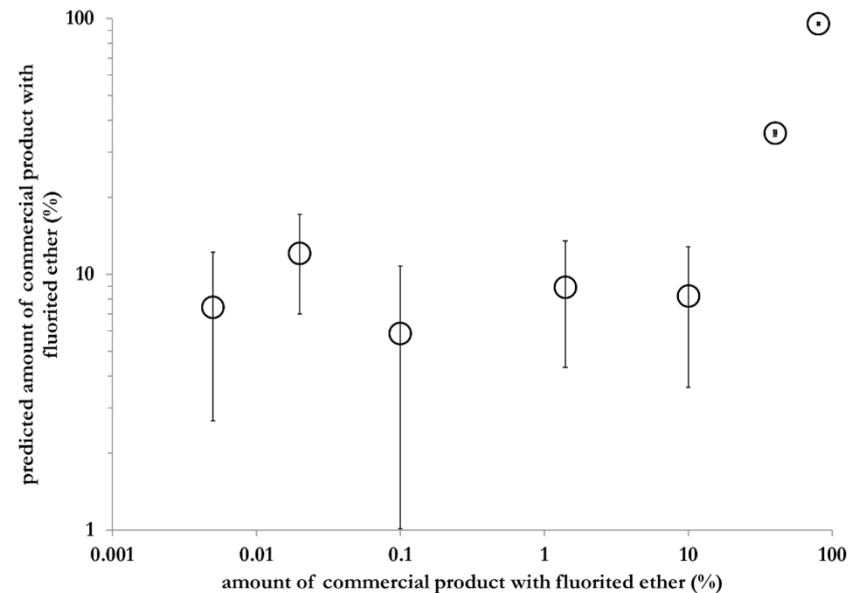
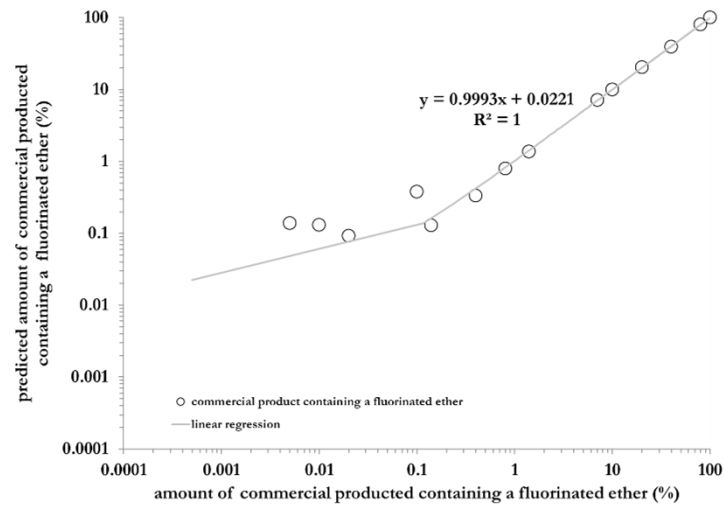
Principal Components Analysis (PCA) on Raman data of tested fluids (type I, II and IV and Cryotech BX36) at different dilutions



Specific case of airports

Raman data and analysis on airports fluids

PLS forecast the amount of fluorinated ether into water



Detection of fluorinated ether threshold:

0.08% (v/v) of commercial solution

Hypothesis of 1% of fluorinated ether

⇒ **detection threshold of 10 ppm**

Ions related to urban configurations

Context and objective

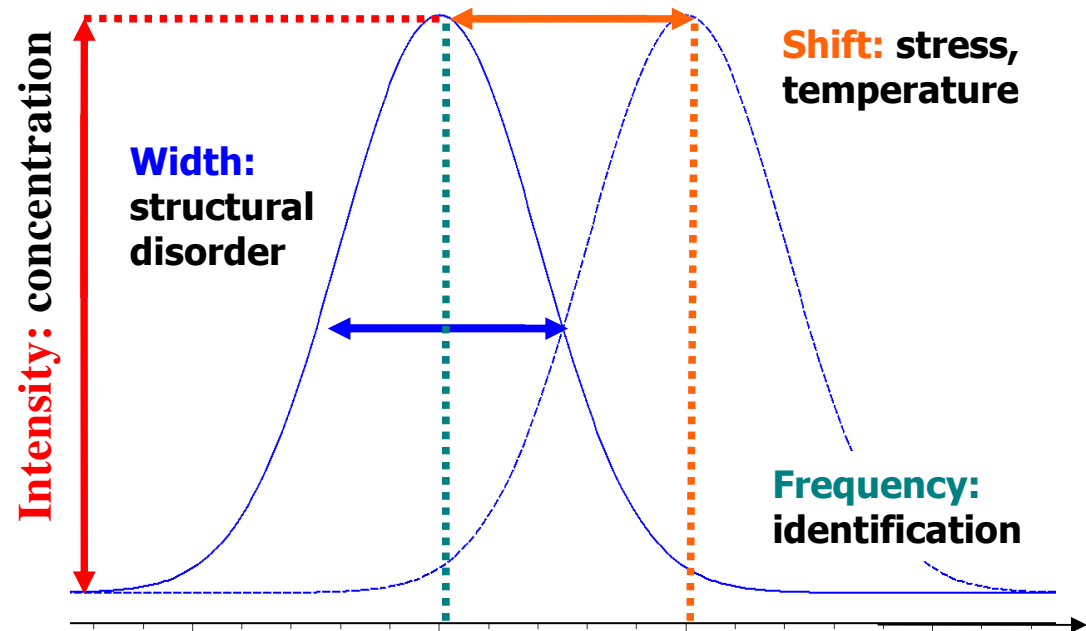
Ecological water balance compromised par presence of anthropogenic species (potability thresholds (mg/L), European directive 98/83/CE)

Objective: to test a method based on Raman spectroscopy (stand alone, chemometrics-coupled) to obtain qualitative and quantitative information on chemical species present into water



Chlorure	Cl ⁻	250
Fluorure	F ⁻	1,5
Nitrate	NO ₃ ⁻	50
Sulfate	SO ₄ ²⁻	250
Nitrite	NO ₂ ⁻	0,1
Sodium	Na ⁺	150
Potassium	K ⁺	12
Magnésium	Mg ²⁺	50
Ammonium	NH ₄ ⁺	0,5

Both use of direct and indirect information from Raman spectra

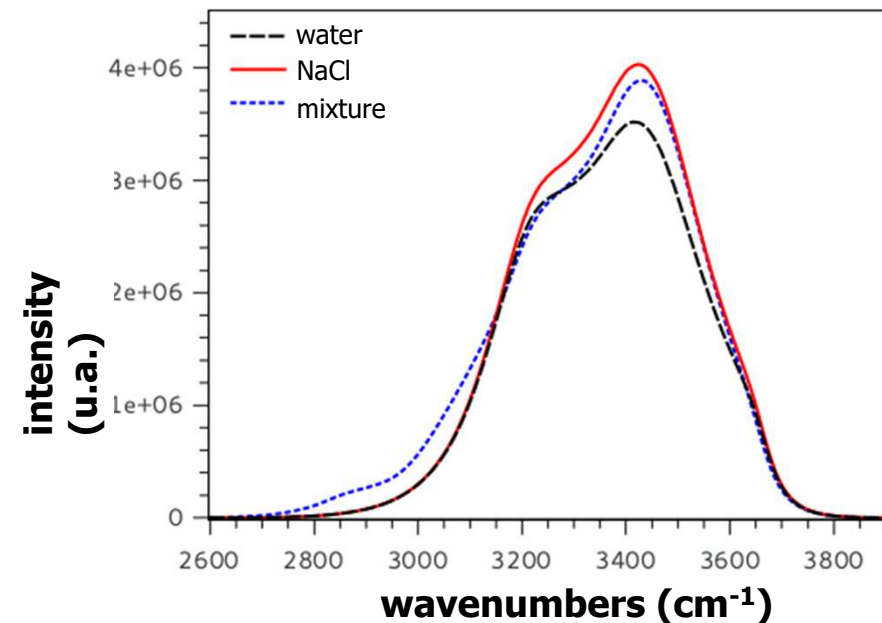
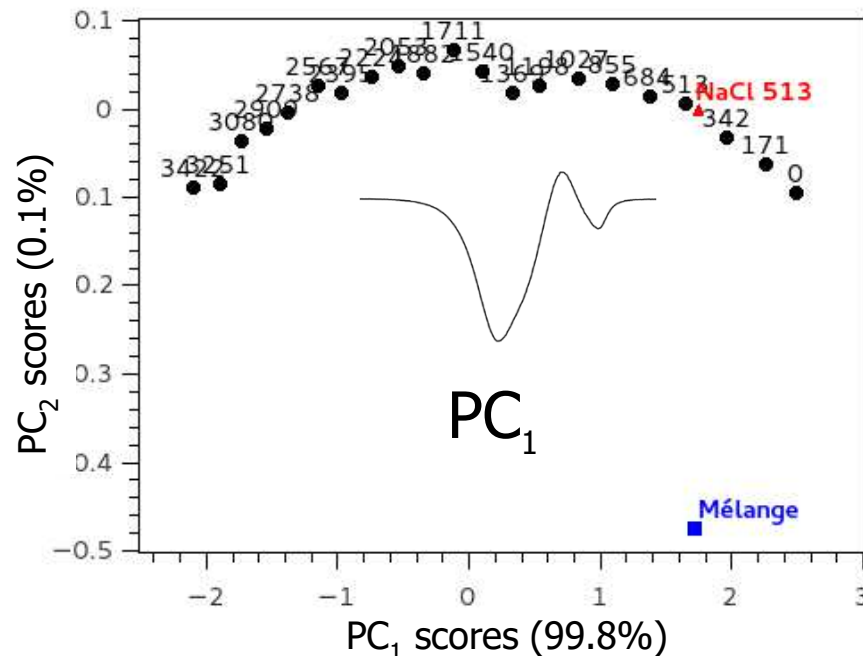


Ions related to urban configurations

Raman data and chemometrics

Raman acquisition with Kaiser RXN-1, laser at 532 nm (300 mW), 100–4350 cm^{-1} (spectral resolution $\sim 2 \text{ cm}^{-1}$), CCD 1024 x 256 cooled at -40°C , integration time 3x5 s)

Case of chloride ion into a mixture



solution	$[\text{Cl}^-]$	forecast $[\text{Cl}^-]$
NaCl pure	513 mM	412 mM ($\epsilon = 20\%$)
mixture	513 mM	436 mM ($\epsilon = 15\%$)

Ions related to urban configurations

Raman data and chemometrics

Case of mixtures

Solutions	[NO ₃ ⁻]	[SO ₄ ²⁻]	[Cl ⁻]	[Br ⁻]	[I ⁻]	[NH ₄ ⁺]
Nitrate à 90 mM	91	0	0	0	0	0
Nitrate à 50 mM	49	0	0	0	0	0
Sulfate à 30 mM	0	32	10	0	15	0
Sulfate à 70 mM	0	72	0	0	0	0
Chlorures à 50 mM	0	0	49	0	0	0
Chlorures à 90 mM	0	25	112	0	0	0
Bromure à 30 mM	0	0	38	0	18	0
Bromure à 90 mM	0	0	0	82	0	55
Iodure à 30 mM	0	0	0	0	28	18
Iodure à 60 mM	0	0	0	77	0	26
Ammonium à 500 mM	0	0	453	0	0	501
Ammonium à 1000 mM	992	0	0	0	0	1011

✓ good results for simple solutions

~ improvements needed with mixtures

predicted concentrations

Solutions	[NO ₃ ⁻]	[SO ₄ ²⁻]	[Cl ⁻]	[Br ⁻]	[I ⁻]	[NH ₄ ⁺]
N80/S20	95	20	X	212	X	42
N50/S50	63	60	X	199	X	44
N20/Cl80	32	X	X	232	X	48
N50/Cl50	63	X	X	210	X	54
Cl70/Br50/I30	9	X	X	359	6	113
Cl50/Br50/I50	8	X	X	430	8	128
N82/S16/Cl33/Br33/I33/NH ₄ 66	97	17	X	335	1	165
N66/S33/Cl33/Br33/I33/NH ₄ 33	78	38	X	314	X	153

Down to water courses

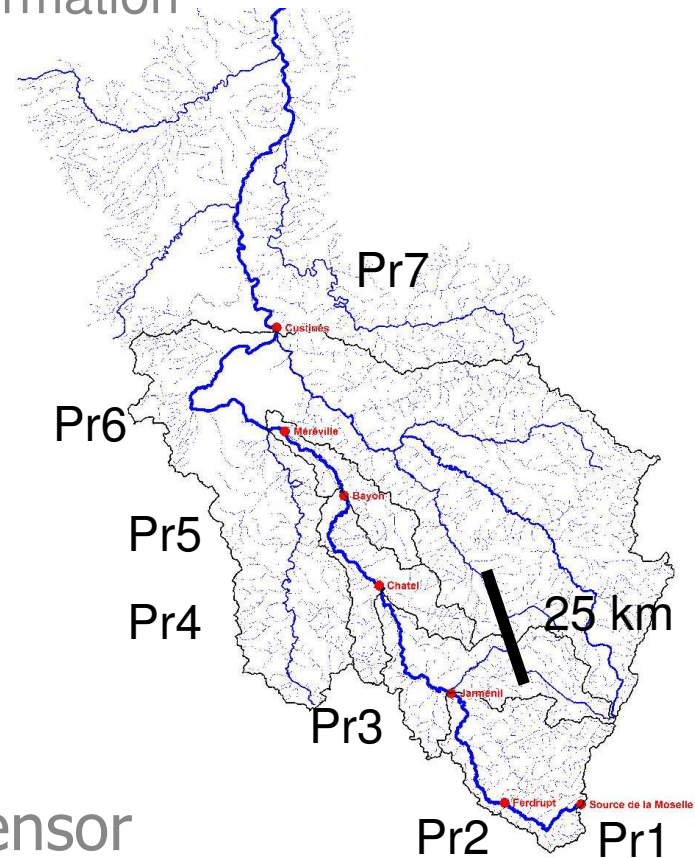
Objective: test on a full scale a Raman-based alternative method to obtain qualitative and quantitative information on water quality variations

Monitoring of a river from the spring to the confluence with another river
Sampling on 7 spots, every month, over two years

Measurements with an i-Raman (BWTek)
532 nm, integration time of a few seconds

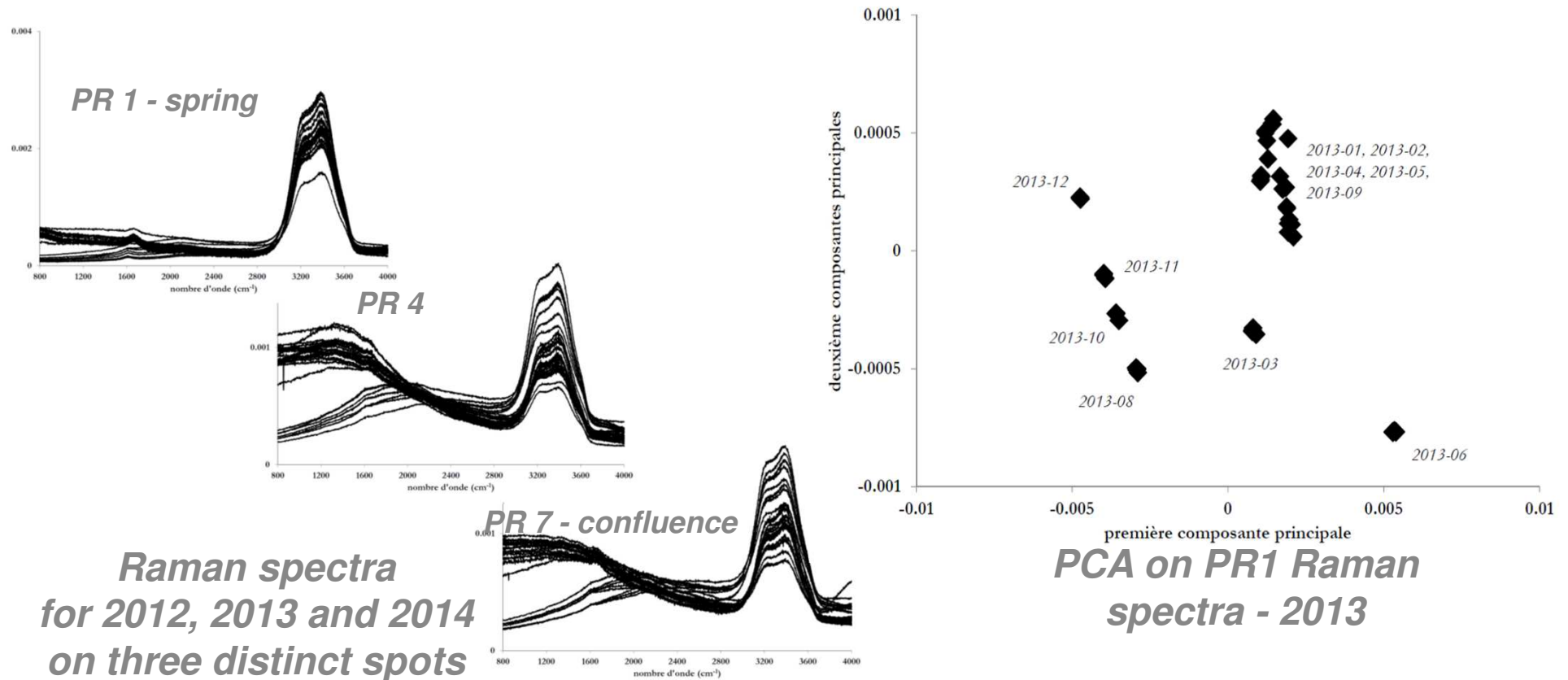
PCA applied to Raman spectra

⇒ reach a cost effective water quality sensor



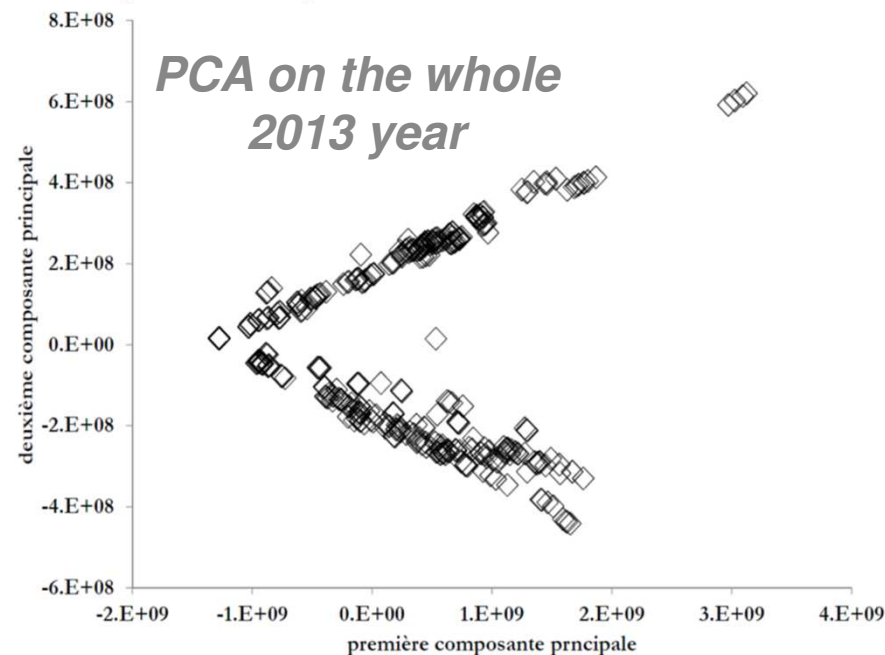
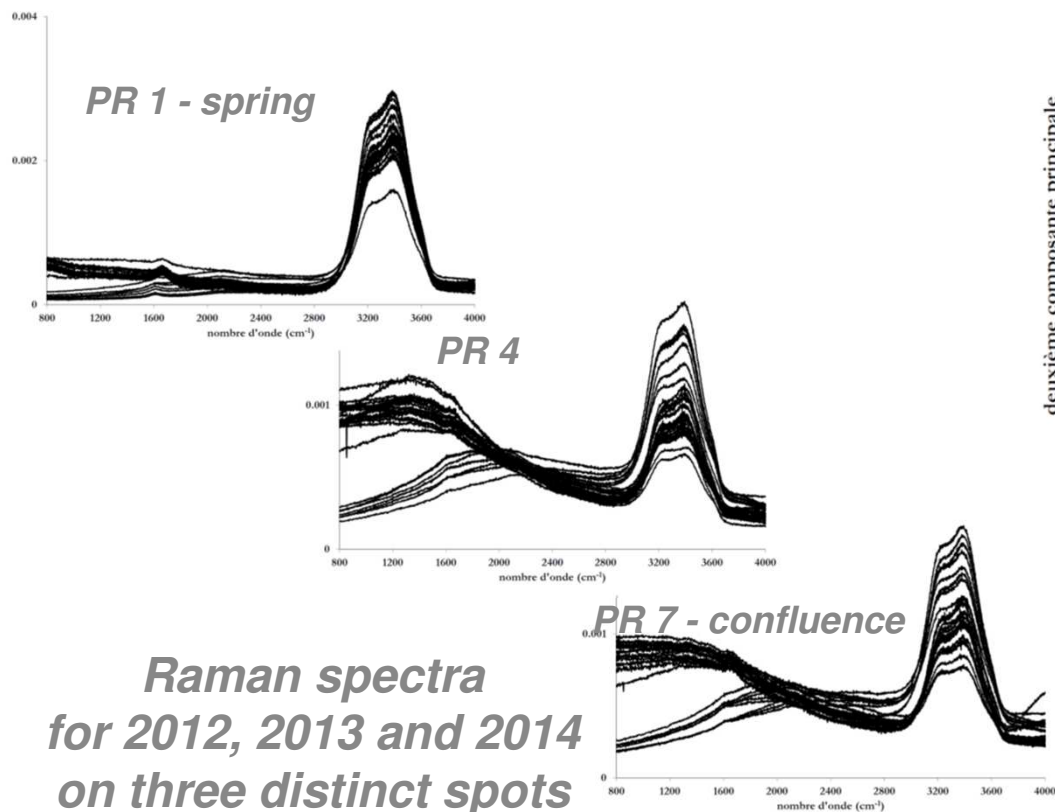
Down to water courses

Evolution with time of water quality



Down to water courses

Evolution with time of water quality

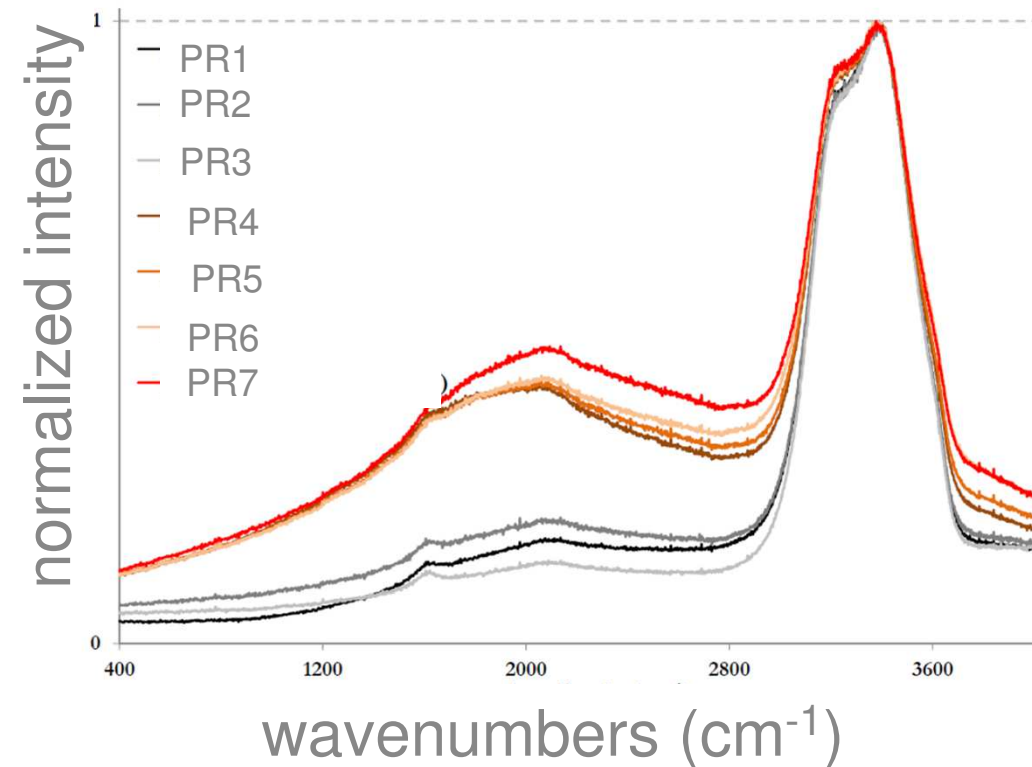


⇒ evolution in water quality

Down to water courses

Evolution along the water course

- the farther from the spring, the greater the fluorescence,
- changes in the 800-1700 cm^{-1} , and 2800-3600 cm^{-1} spectral ranges



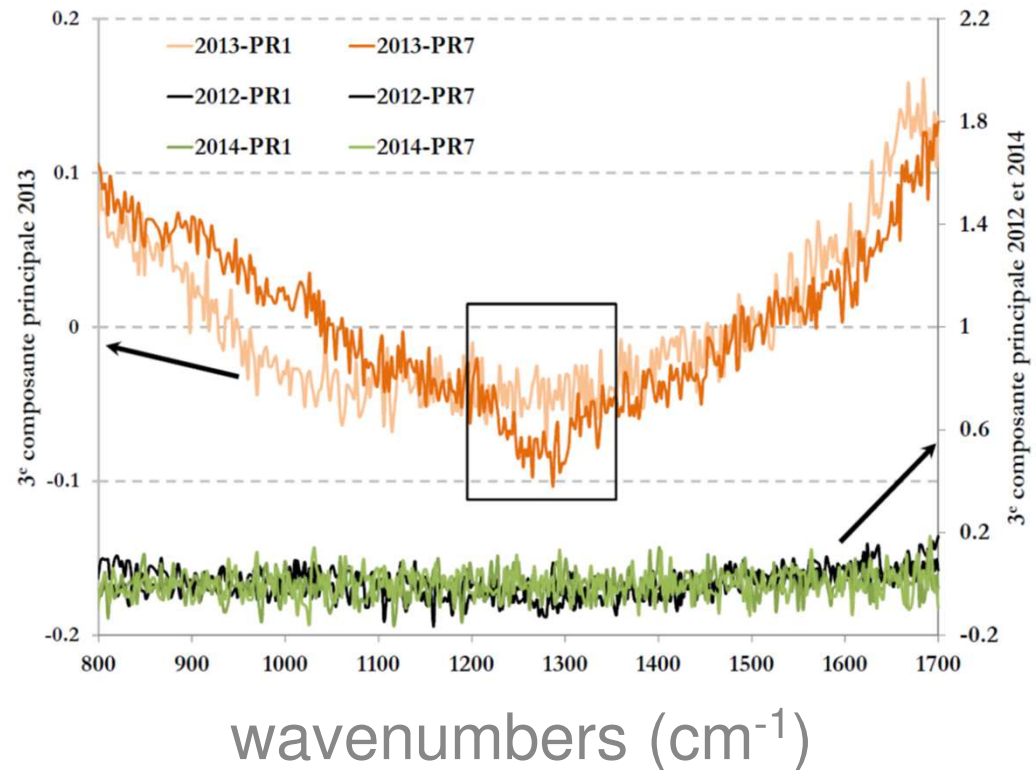
Down to water courses

Evolution along the water course

Comparison between the spring and the confluence

⇒ specificity in a loading in 2013

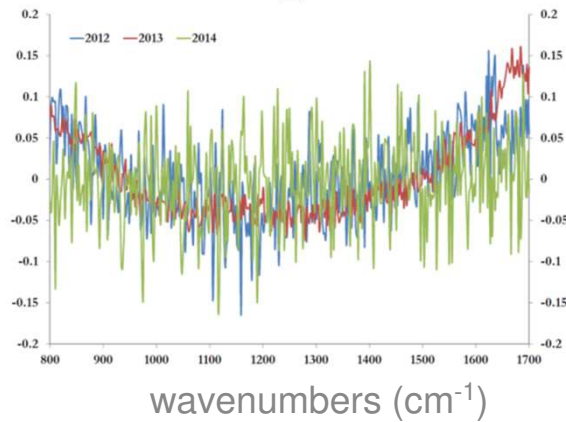
Where is water quality started to change ?



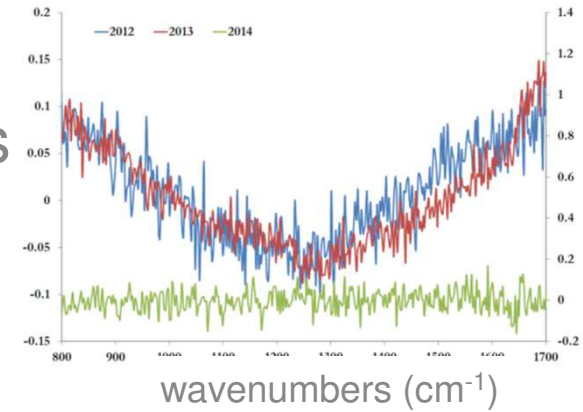
Down to water courses

Evolution along the water course

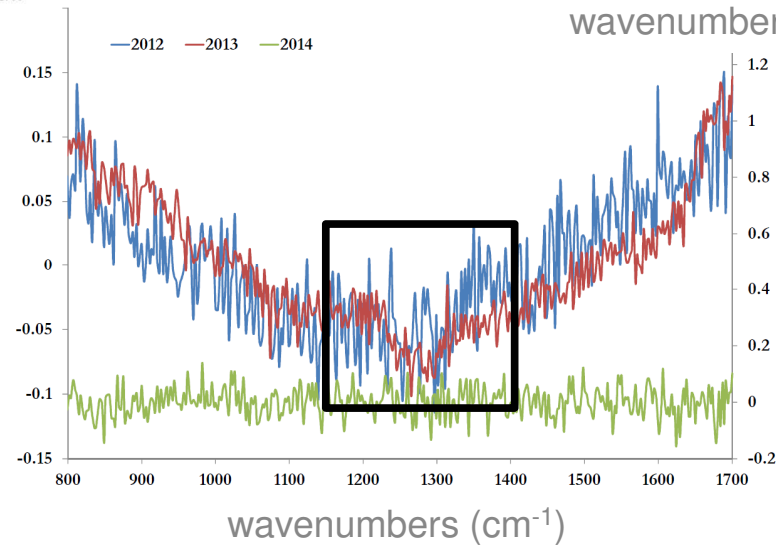
PR1
loadings



PR2
loadings



PR3
loadings



Conclusion

Application of Raman spectroscopy in different applied contexts and in field configurations

Possible detection and quantification into water of some chemicals related to transportation infrastructures (roads, airports, ...)

Extended possibilities, from elaborated Raman spectrometer up to field designed instruments





Thanks for your attention

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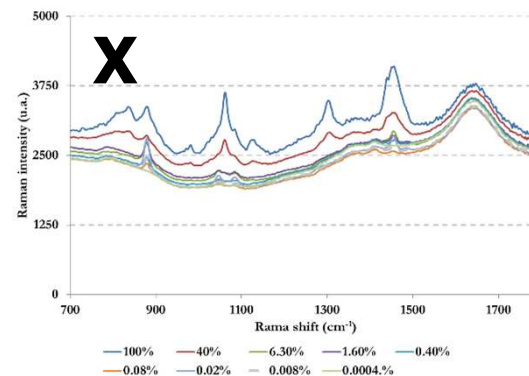
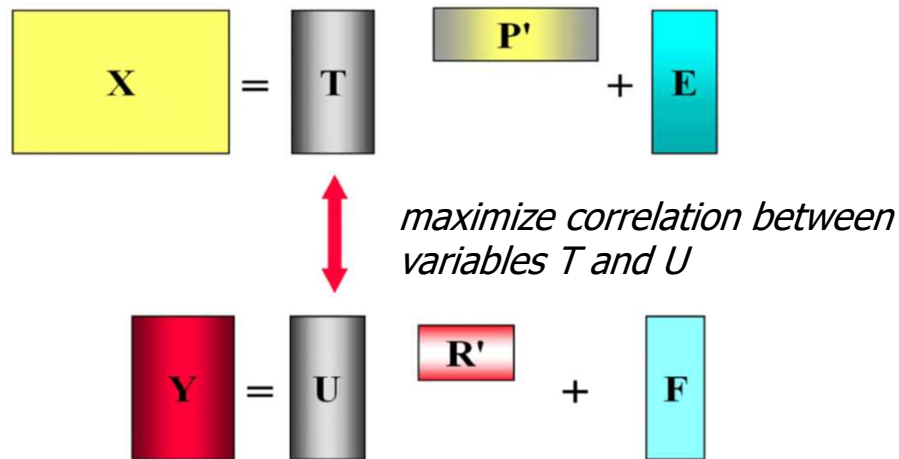
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Specific case of airports

Raman data and analysis on anti-icing fluids

PLS forecast the amount of fluorinated ether into water



Y

C_1
 C_2
...
...
...
...
 C_n

X = matrix of Raman spectra of solutions with decreasing concentration in fluorinated ether (no significant difference on normalized spectra)

Y = matrix of concentration

Ions related to urban configurations

Context and objective

Ecological water balance compromised par presence of anthropic species

Products and chemicals ending up into the environment, with mobilisation of other pollutants

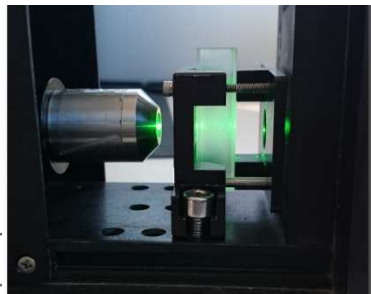
Water quality appreciation based on field conventional measurements (pH, conductivity, suspended matter, NO_3^- ...) and collected samples for further laboratory analysis (dosing, chromatography, ...)

Main drawbacks and limits: analysis on a given spot, delay between sample collection and information

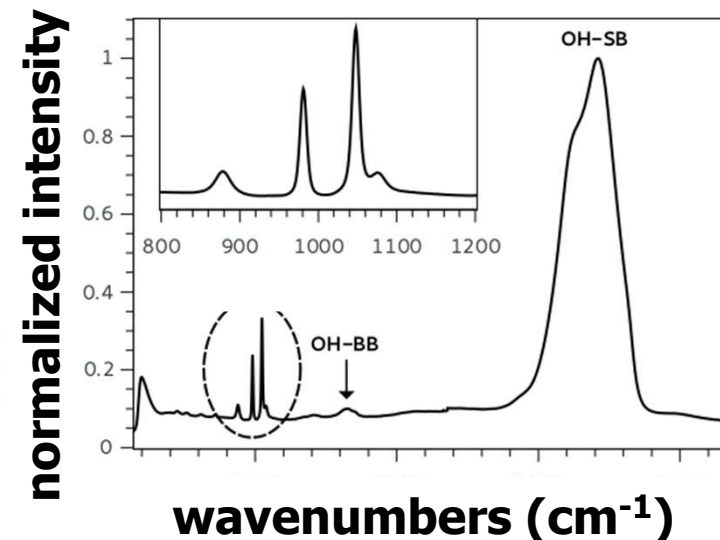
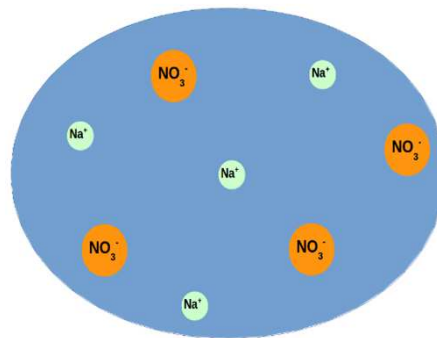
Ions related to urban configurations

Raman data and analysis of specific peaks

Raman acquisition with Kaiser RXN-1, laser at 532 nm (300 mW), 100 – 4350 cm⁻¹ (spectral resolution ~2 cm⁻¹), CCD 1024 x 256 cooled at -40°C, integration time 3x5 s)



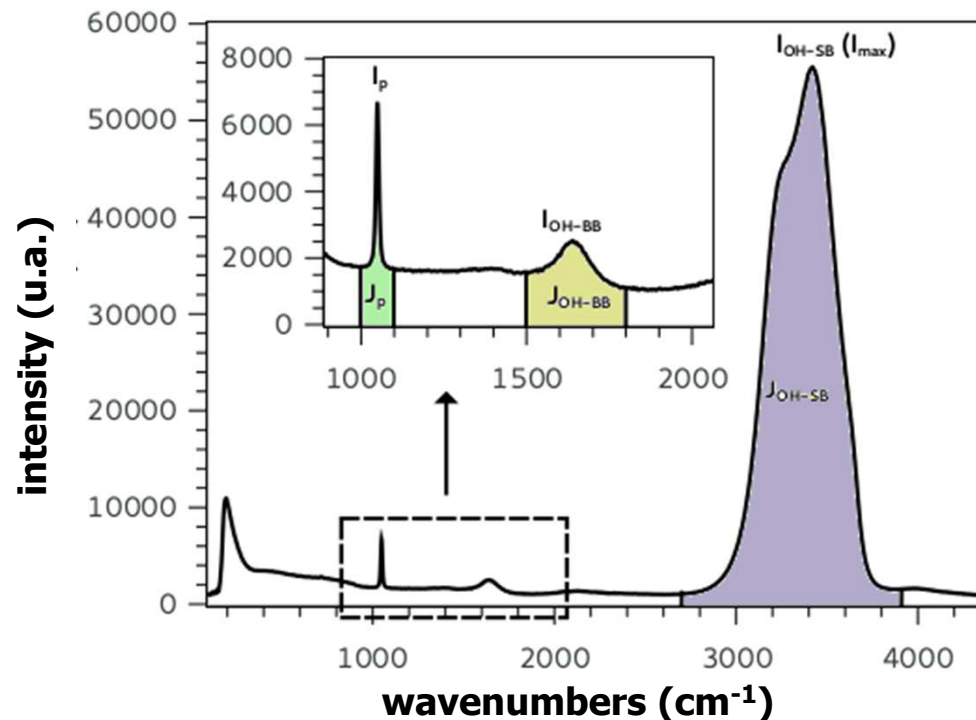
Ion	Position
NO ₃ ⁻	1047 cm ⁻¹
SO ₄ ²⁻	981 cm ⁻¹
HPO ₄ ²⁻	990 cm ⁻¹
NO ₂ ⁻	816 - 1330 cm ⁻¹
SO ₃ ⁻	966 cm ⁻¹



Ions related to urban configurations

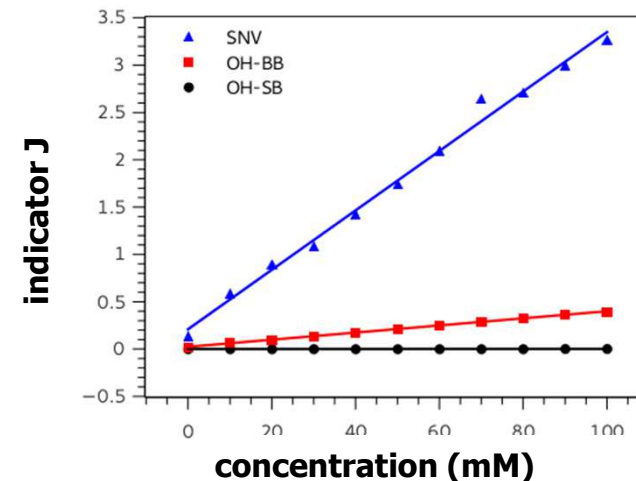
Raman data and analysis of specific peaks

Quantification through indicators (data processing and sensitivity)



Normalization

- **OH-BB band:** $J_p^{OH-BB} = J_p / J_{OH-BB}$
- **OH-SB band:** $J_p^{OH-SB} = J_p / J_{OH-SB}$
- **SNV:** $J_p^{SNV} = (J_p - \bar{J}) / \sigma_J$



Ions related to urban configurations

Raman data and analysis of specific peaks

Quantification through indicators (data processing and sensitivity)

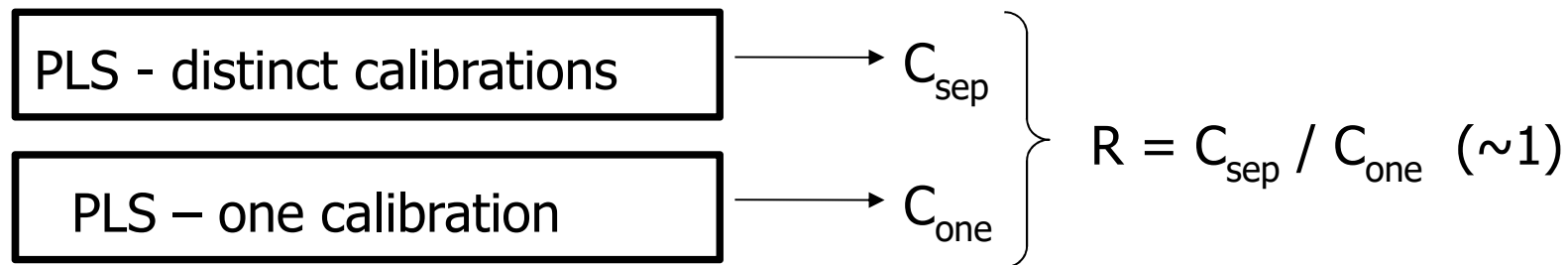
normalization methods	R ²	sensitivity S
Spectra	0,9571	$1,6 \times 10^3$ u.a./mM
OH stretching J_p^{OH-SB}	0,9926	$1,8 \times 10^{-5}$ mM ⁻¹
OH bending J_p^{OH-BB}	0,9980	$3,8 \times 10^{-3}$ mM ⁻¹
SNV J_p^{SNV}	0,9924	$3,1 \times 10^{-2}$ mM ⁻¹

sensitivity	S	$3,11 \times 10^{-2}$ mM ⁻¹
average error	ε	4,2 mM
average quadratic error	RMSE	5,2 mM
repetability (n=30)	CV	3,9 %
limit of détection (k=3)	LD	1,8 mM (112 mg/L)
Limit of quantification	LQ	5,9 mM (366 mg/L)

Ions related to urban configurations

Raman data and chemometrics

Case of mixtures



$$C_{sep} < 0 \text{ ou } C_{uni} < 0 \Rightarrow C_{pred} = 0$$

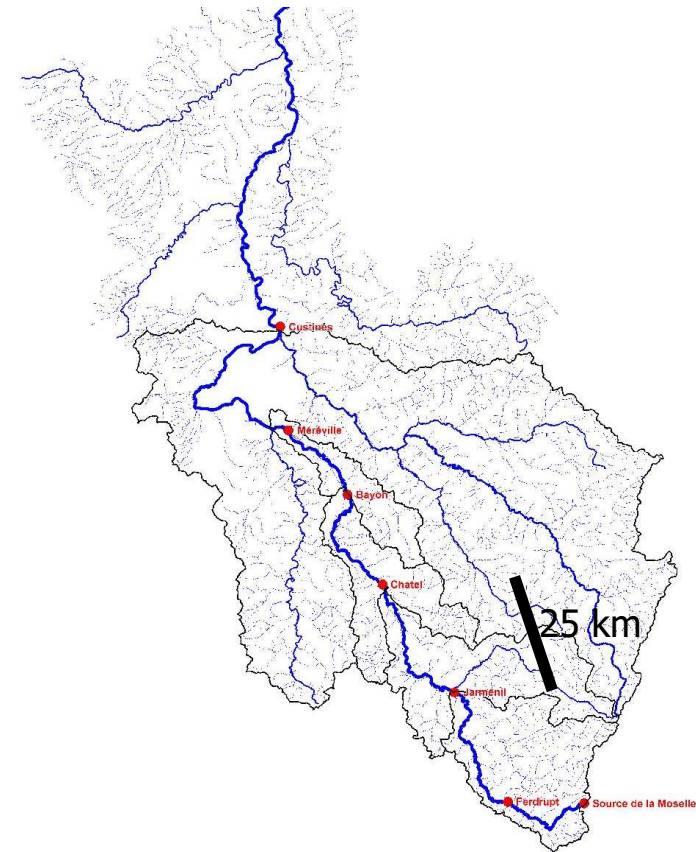
$$0,5 < R < 2 \Rightarrow C_{pred} = C_{sep} \text{ (accuracy gain)}$$

Down to water courses

Water quality analysis based on conventional techniques (pH, suspended matter, NO_3^- ...) and sampling with later lab tests (dosing, chromatography, ...)

Main drawbacks: analysis in specific spots, results obtained afterwards

Objective: test on a full scale a Raman-based alternative method to obtain qualitative and quantitative information on water quality variations between different spots and in time



Moselle river (north east of France)