

Colloque annuel du PIREN-Seine

5 & 6 octobre 2017

Evaluer le devenir des nanoparticules dans les écosystèmes aquatiques

Jialan Wang^{1,2}, Enrica Alasonati², Alexandre Gélabert¹, Yann Sivry¹, Paola Fisicaro², Marc F. Benedetti^{1,*}

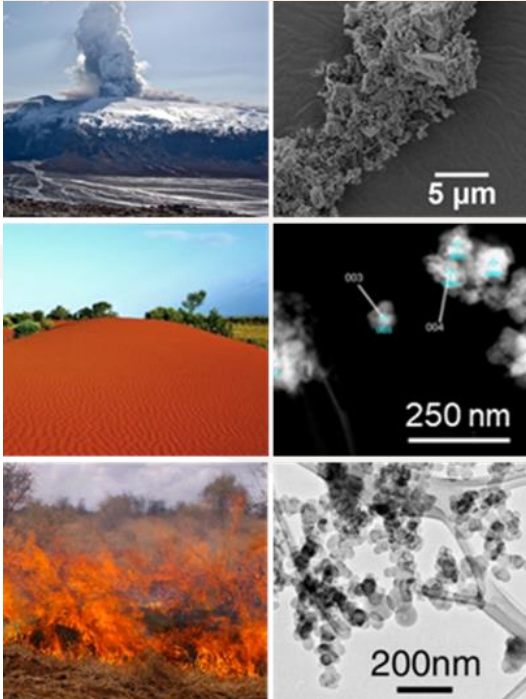
¹ Institut de Physique du Globe de Paris, Université Paris Diderot, Sorbonne Paris Cité, Institut de Physique du Globe de Paris, UMR 7154 CNRS, Paris

² Département Biomédical et Chimie Inorganique, Direction Métrologie Scientifique et Industrielle, Laboratoire national de métrologie et d'essais, Paris

*benedetti@ipgp.fr

Sources de NPs

Natural



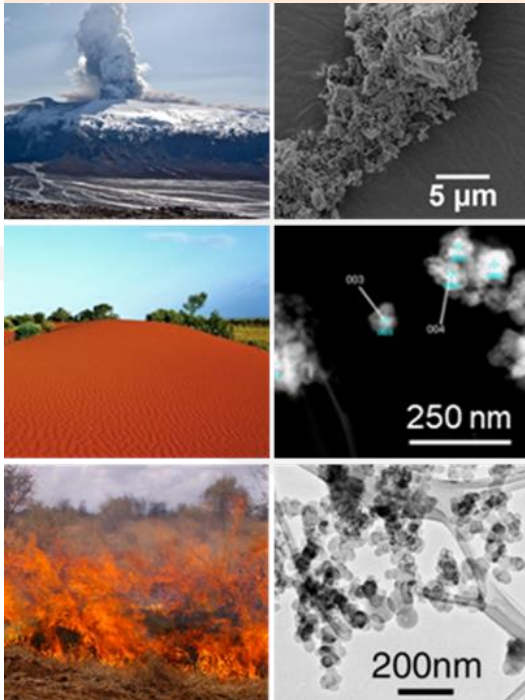
- volcanic activity
- deserts
- bushfires
- microbial processes



Sources de NPs

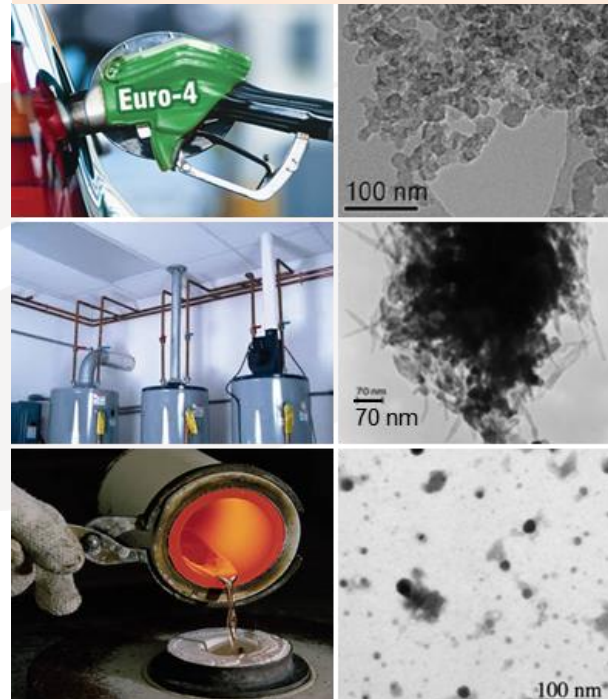
Anthropogenic

Natural



- volcanic activity
- deserts
- bushfires
- microbial processes

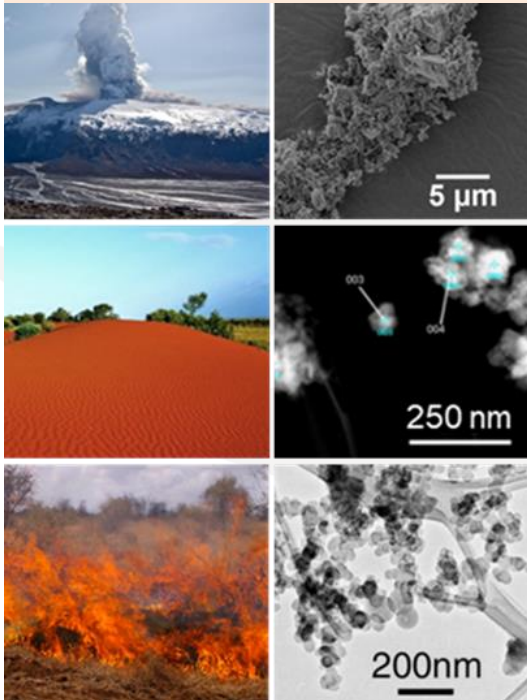
Accidental



- fossil fuel combustion
- mining metal refinery activity
- large-scale demolitions
- household activities

Sources de NPs

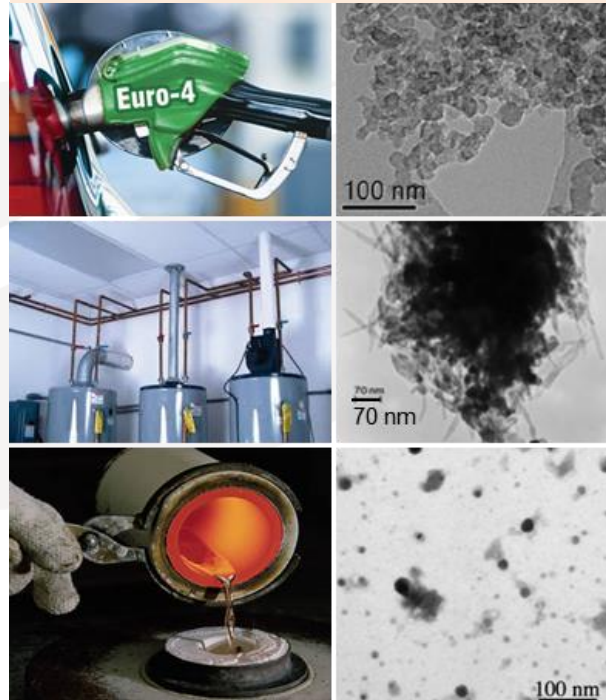
Natural



- volcanic activity
- deserts
- bushfires
- microbial processes

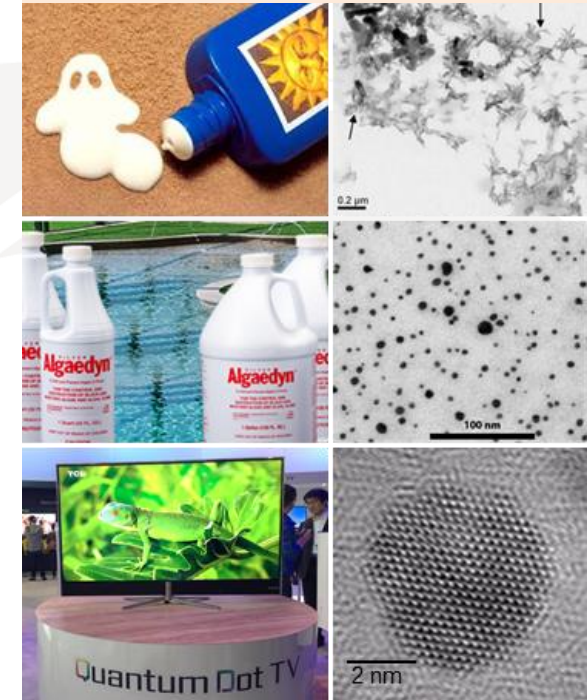
Anthropogenic

Accidental



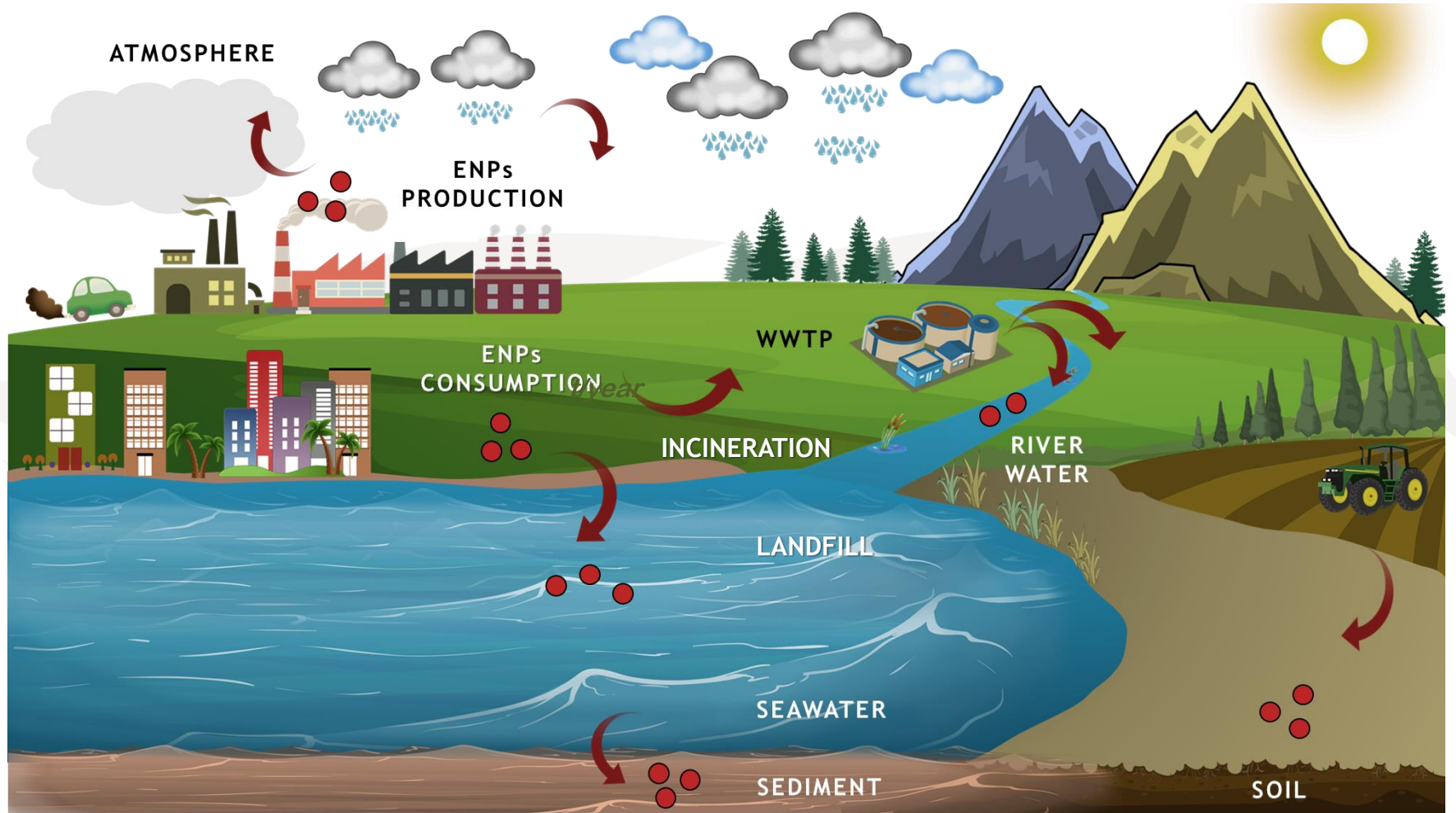
- fossil fuel combustion
- mining metal refinery activity
- large-scale demolitions
- household activities

Engineered (ENPs)

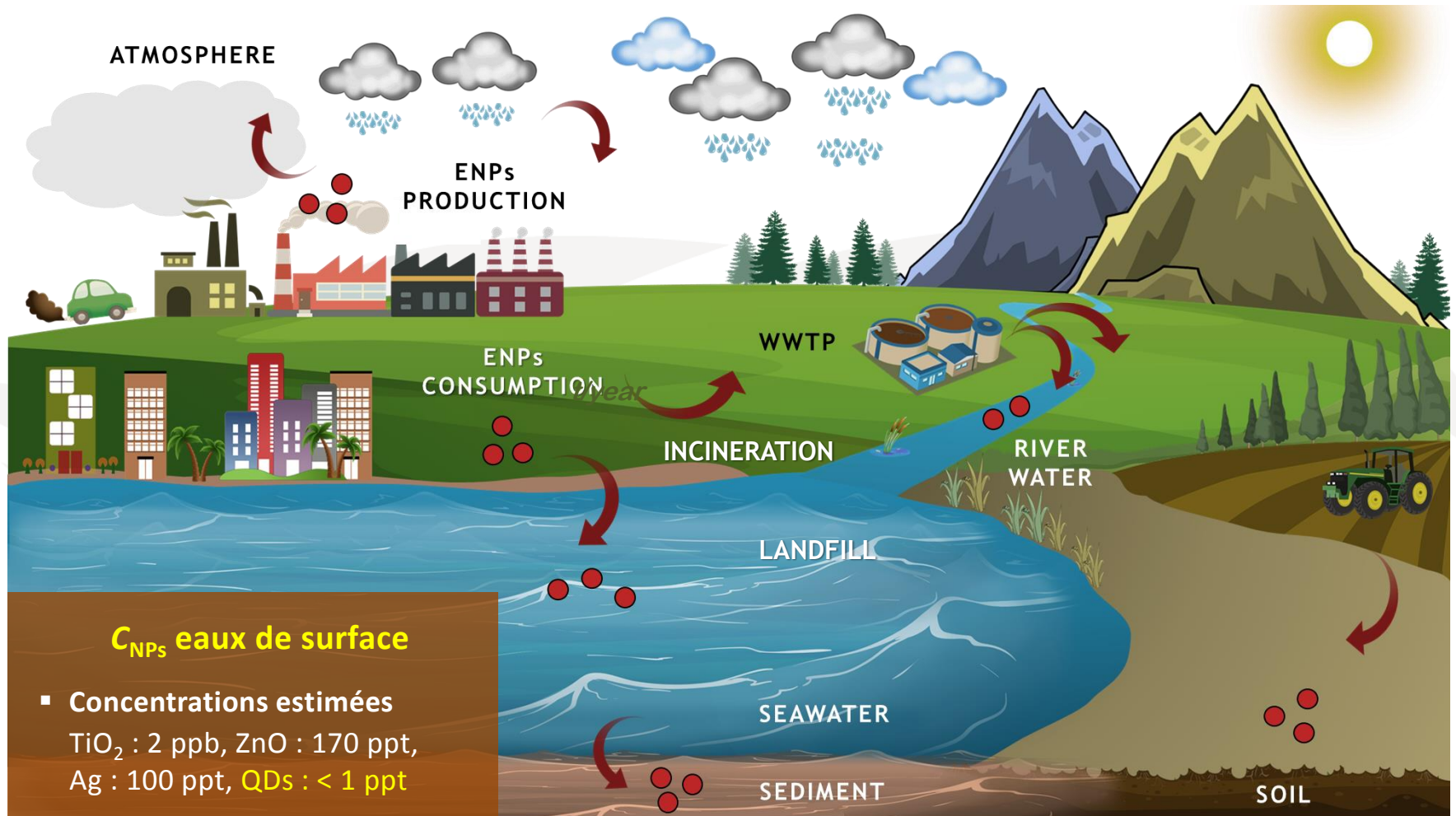


- sunscreen
- algicide
- electronic devices
- waste incineration

NPs dans l'environnement



NPs dans l'environnement



C_{NPs} eaux de surface

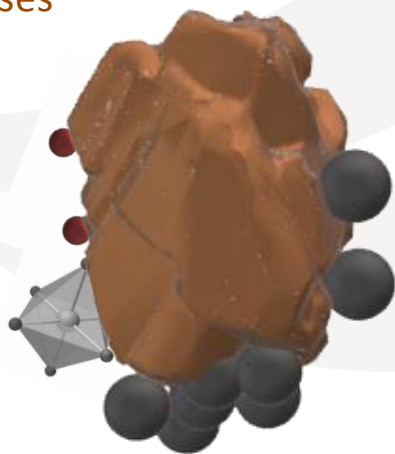
- Concentrations estimées
TiO₂ : 2 ppb, ZnO : 170 ppt,
Ag : 100 ppt, QDs : < 1 ppt

*Gottschalk et al., 2015,
Piccinno et al., 2012*

Transformations dans l'environnement

heteroaggregation

mineral/organic phases



ENPs



dissolution



precipitation



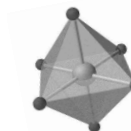
M-L (s)
e.g. $ZnCO_3 (s)$

Sivry et al. 2014

homo-aggregation



complexation



M-L
e.g. CdTGA

sedimentation



Objectifs

- Peut-on détecter, compter et mesurer les NPs dans les rivières ?
- Peut-on déterminer l'origine de ces NPs ?
- Peut-il y avoir un effet du type d'usage des sols sur le type de NPs et leur flux?



Thèse préparée
à l'INSTITUT DE PHYSIQUE DU GLOBE DE PARIS
École Doctorale STEPUP - ED N°560
IPGP - Equipe de Géochimie des Eaux

**Détection et quantification de nanomatériaux
dans les eaux naturelles par une approche
intégrée multi outils**

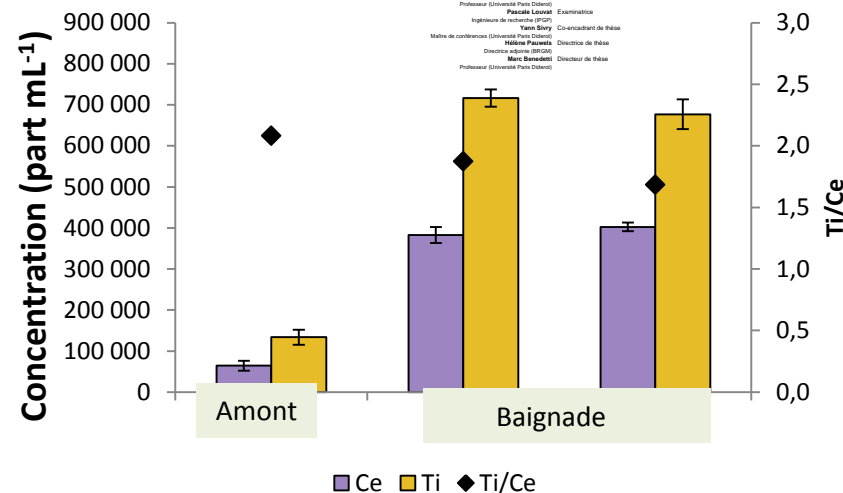
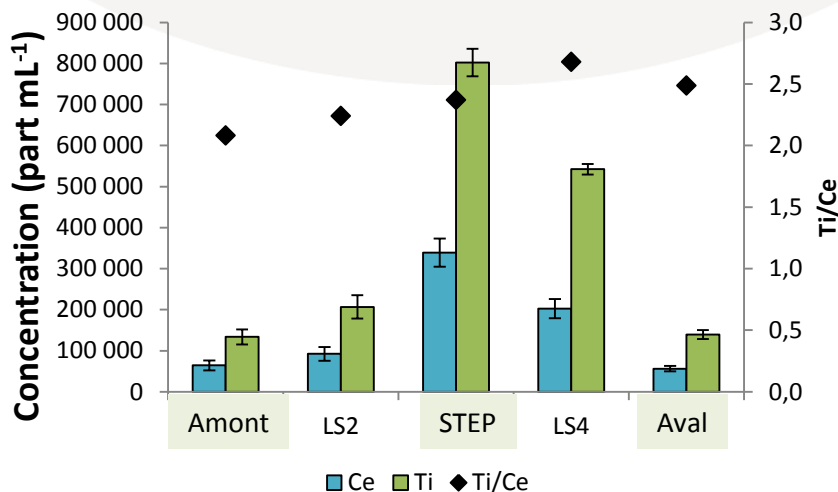
par
Karine Phalyvong

présentée et soutenue publiquement le
18 Novembre 2016

Thèse de doctorat de Sciences de la Terre et de l'environnement
dirigée par Marc Benedetti
& Hélène Pauwels & Yann Sirey

devant un jury composé de :

David Cornille (Rapporteur)
(Swedish Agricultural University, Sweden)
Sébastien Loubès (Rapporteur)
Chargé de recherche (Au-Marseille Université)
Jean-Yves Pignatelli (Examinateur)
Professeur (Université Paris Diderot)
Francis Lesautour (Examinateur)
Ingénieur de recherche (IPGP)
Yann Sirey (Co-encadrant de thèse)
Maître de conférences (Université Paris Diderot)
Hélène Pauwels (Directrice de thèse)
Dorothea Schuster (IPGP)
Marc Benedetti (Directeur de thèse)
Professeur (Université Paris Diderot)



Sites / prélèvements

Thèse préparée
à l'INSTITUT DE PHYSIQUE DU GLOBE DE PARIS
École doctorale STEP'UP – ED N°560
IPGP – Équipe de Géochimie des Eaux

L'origine des métaux et la dynamique du zinc dans le bassin de la Seine

par
Caroline BONNOT

présentée et soutenue publiquement le
26 juin 2015

Thèse de doctorat de Sciences de la Terre et de l'Environnement
dirigée par Marc BENEDETTI

devant un jury composé de :

Françoise ELBAZ-POULICHET Directeur de recherche (Université de Montpellier)	Rapporteur
Géraldine SARRET Directeur de recherche (Université de Grenoble)	Rapporteur
Jean-Marie MOUCHEL Professeur (Université Pierre et Marie Curie)	Examinateur
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Alexandre GÉLABERT Maître de conférences (Université Paris Diderot)	Co-encadrant
Marc BENEDETTI Professeur (Université Paris Diderot)	Directeur de thèse

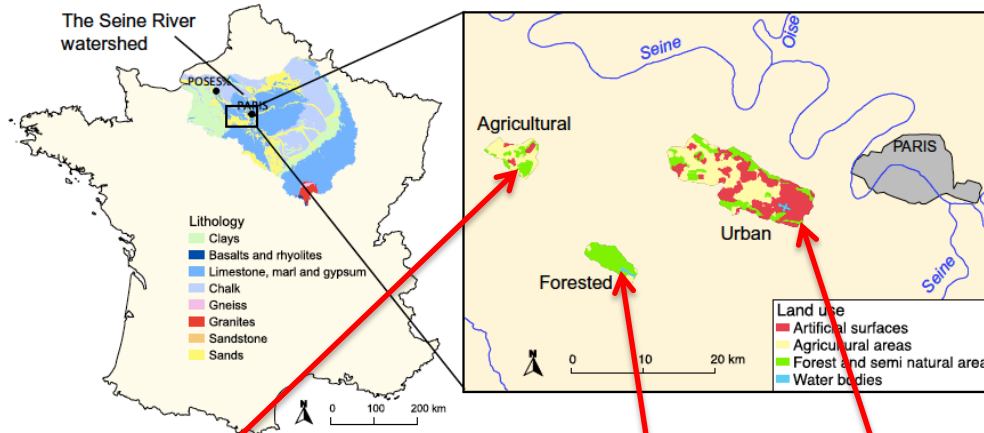
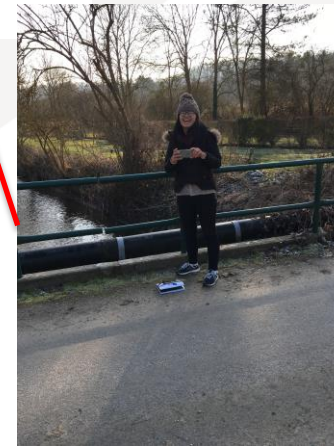


Fig. 1 Location, lithology, and land use of the three characteristic sub-basins in the Seine River watershed, France



	Urban	Agriculture	Forest
Area (km ²)	116	22	17
Artificial surfaces	37%	6%	0%
Agricultural areas	44%	72%	5%
Forest and semi natural areas	19%	22%	92%

Argent

NATURE'S SUNSHINE

SILVER SHIELD

Benefits of silver for the skin?

No Silver **With Silver**

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Discover the Source of Cellular Energy
Gold, Silver, Platinum, Magnesium, Iron, Zinc en Copper

Nano Minerals
The Purest Water, the Smallest Particles

Discover Nano

whitening
QZHANFU new breakthrough root touches the skin, three hours white skin pure white and flawless as pearl

moisturizing
Lock the skin moisture, emulsify skin moisturizing formula, quickly penetrate into skin moisture

tender
Effectively repair damaged skin, skin care skin luster, make skin more tender

nourish
Mild and nourishing formula, deeply nourish skin, wake up skin natural vitality.

The elastic
To stimulate new elastic protein, like in the skin the small spring, spring up

QLZHANFU Nano silver whitening and moisturizing hydrating essence capsule carry bright color skin nourish skin facial essence

★★★★★ 5.0 (1 votes) 6 orders

Price: **US \$9.99** / lot 30 pieces / lot, US \$0.34 / piece
Bulk Price ▾

Shipping: **Free Shipping to United States via Singapore Post** ▾
Estimated Delivery Time: **26-44 days** 📦

Quantity: lot (194 lots available)

Total Price: **US \$9.99**

👤 Add to Wish List (36 Adds) ▾

Return Policy: Returns accepted if product not as described, buyer pays return shipping fee; or keep the product & agree refund with seller. [View details](#) ▶

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DELUXE towel

SOCKS

Denti-Baby TOOTHBRUSH

Ultimate Freshness

gem guard cleaning cloth

SILICONE TOOTHBRUSH

SilverCare ANTIBACTERIAL TOOTHBRUSH

Medical Grade Silicon, AG+

Denti-Baby

cor

<http://theconversation.com/nano-silver-in-household-products-could-breed-new-superbugs-3378>

NPs d'Ag



QLZHANFU Nano silver whitening and moisturizing hydrating essence capsule carry bright color skin nourish skin facial essence

★★★★★ 5.0 (1 votes) | 6 orders

Price: **US \$9.99** / lot 30 pieces / lot, US \$0.34 / piece

Bulk Price ▾

moisturizing
Lock the skin moisture, improve skin moisture, function quickly.

whitening
QLZHANFU new breakthrough, root touches the skin, three bran white skin pure white and flawless, no pain.

nourish
Moisturizing



Shipping to United States via Singapore Post ▾

Delivery Time: 26-44 days 🟢

+ lot (194 lots available)

9

Add to Cart

Added ▾

Payments accepted if product not as described, buyer pays return shipping fee; or keep the product & agree refund with seller. details ▾

Free Delivery

Days

View More ▾



Nano Minerals

The Purest Water, the Smallest Particles

Discover Nano

SilverCare[™] ANTIBACTERIAL TOOTHBRUSH

MEDIO/medium

SILICONE

cor

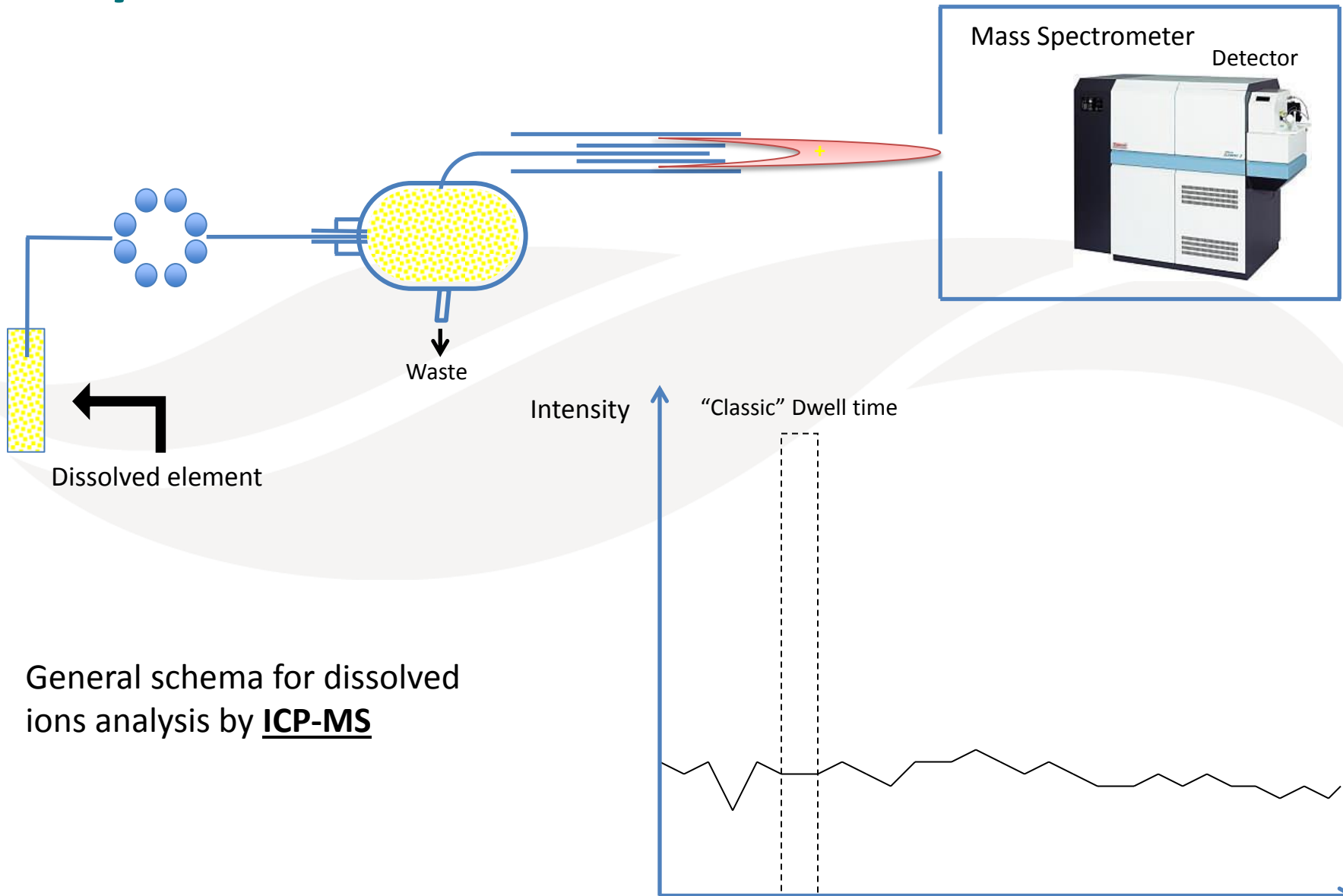
The Silver Soap[™] La Saponi Sargenti[™] 30g x 100

VS SASSON

hairbrush

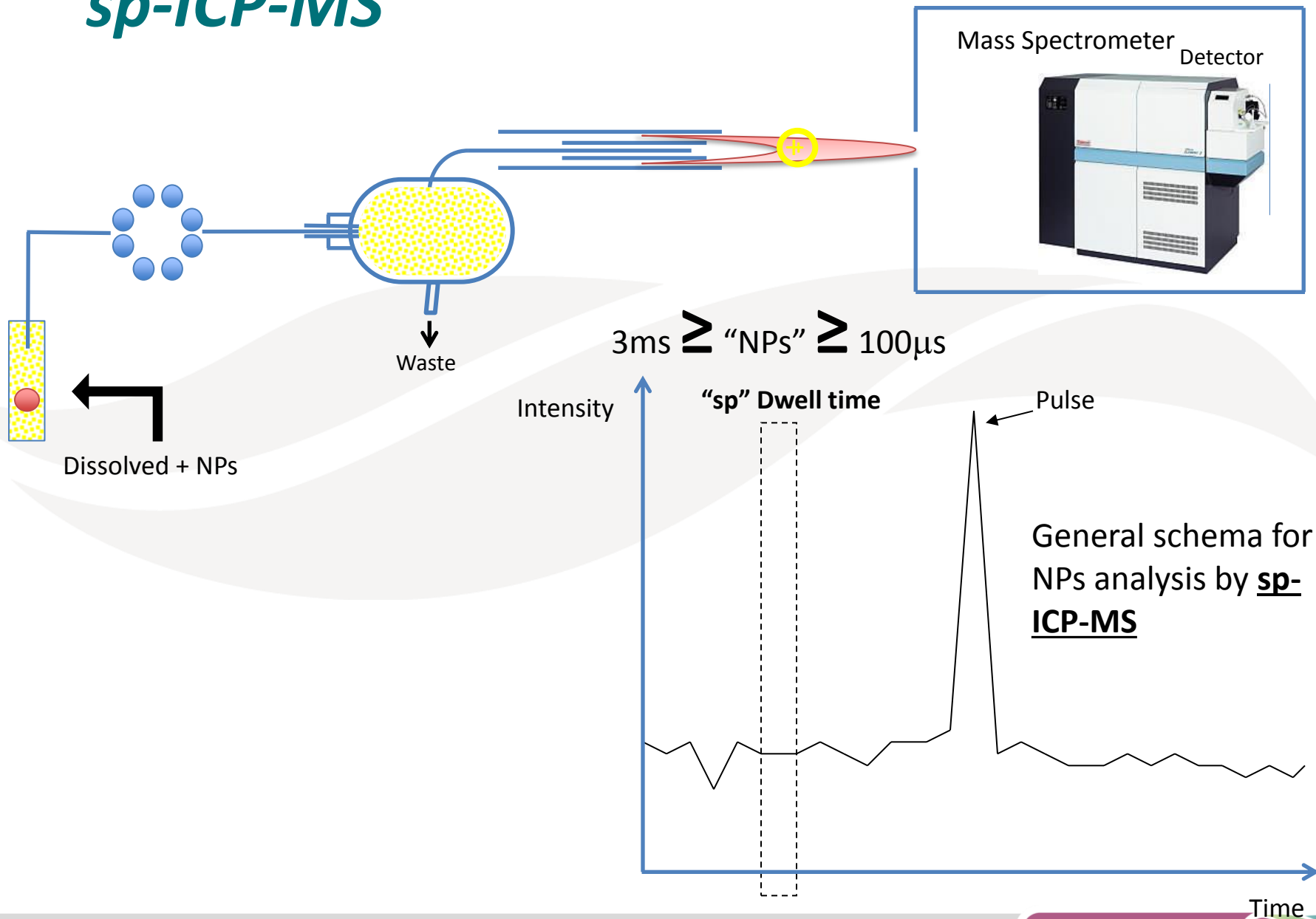
<http://theconversation.com/nano-silver-in-household-products-could-breed-new-superbugs-3378>

sp-ICP-MS

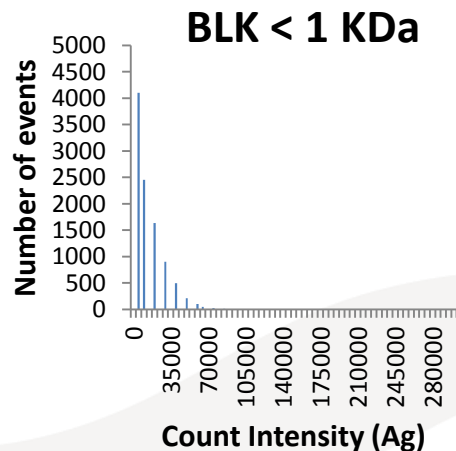


General schema for dissolved ions analysis by **ICP-MS**

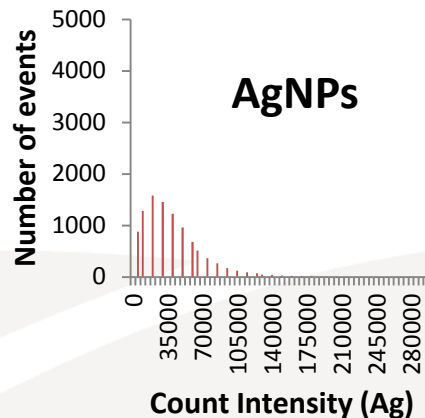
sp-ICP-MS



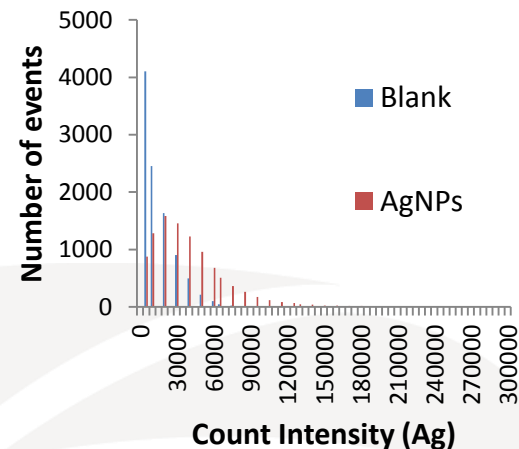
sp-ICP-MS



(Pace *et al.*, 2012)



(Telgmann *et al.*, 2014)

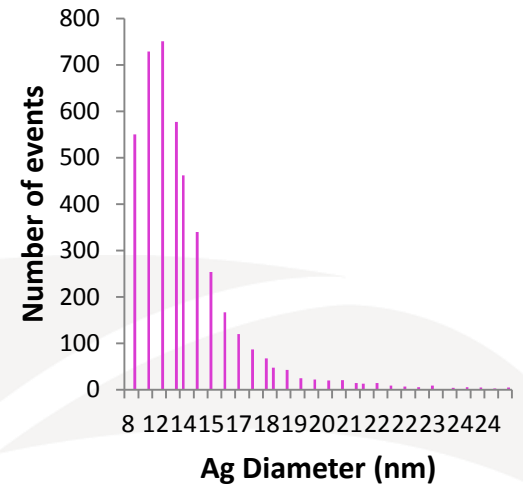
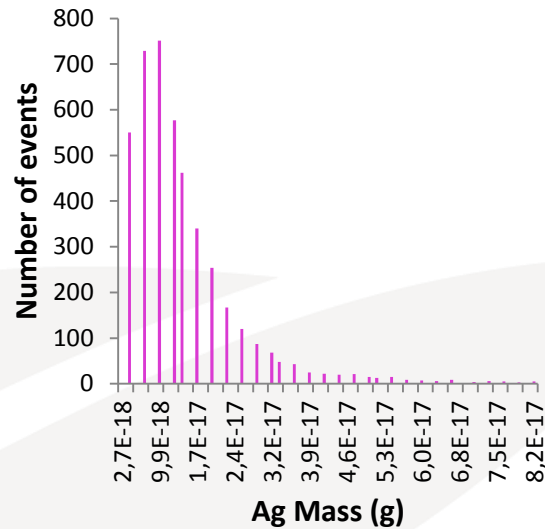
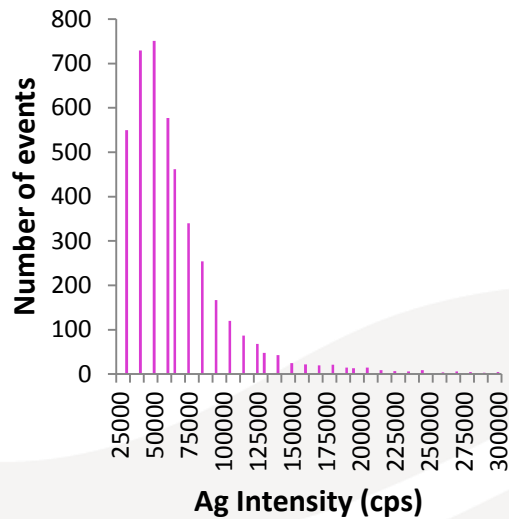


(Hineman and
Stephan, 2014)



- **High dwell time:** increase of particle coincidence, if solutions are not diluted enough
- **Low dwell time:** smaller detected size but higher difficulty to make the difference between dissolved and NPs signals
- **Find a compromise: 1 ms (in our case)**

sp-ICP-MS



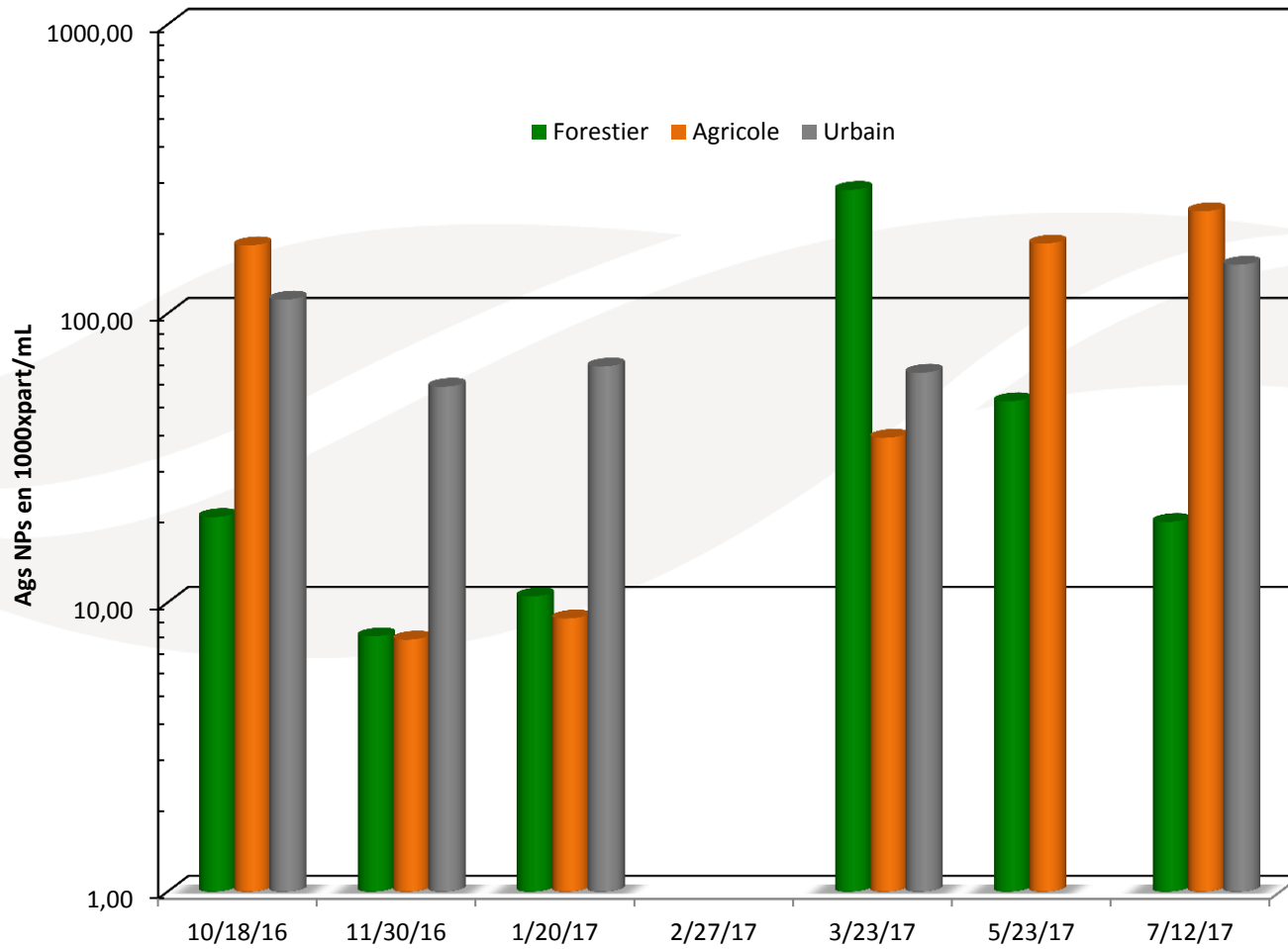
$$N_p = \frac{f(I_p)}{q_{liq} \cdot \eta_n}$$

(Pace et al., 2009)

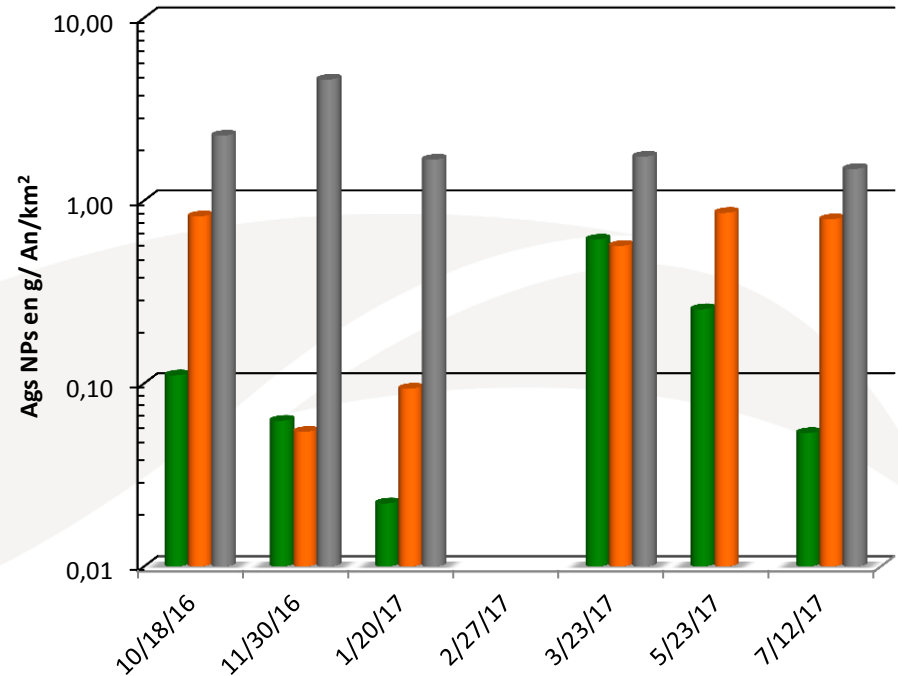
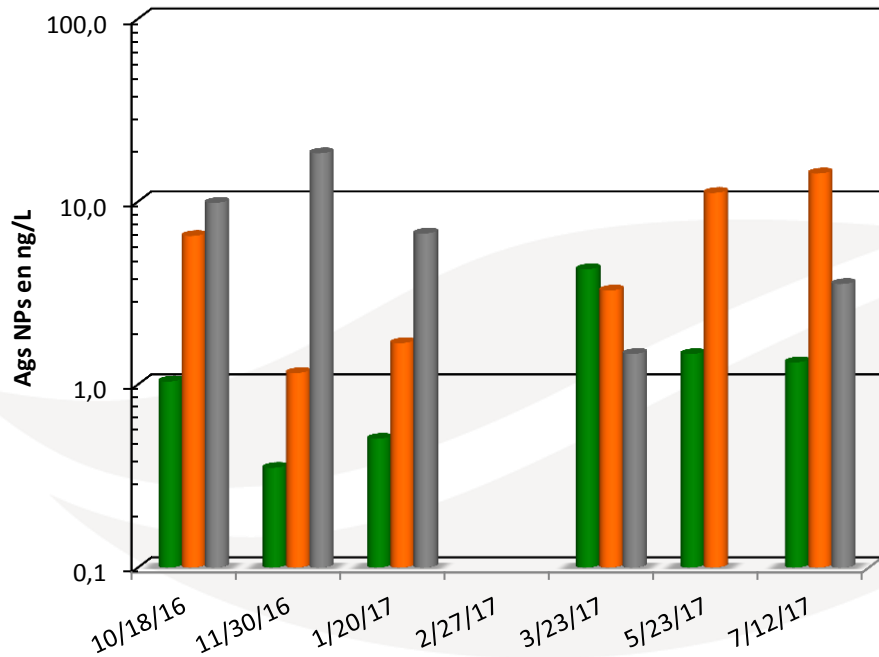
$$m_p = f_a^{-1} \cdot \left[\frac{\left(\frac{I_p - I_{BGD}}{\eta_i} \right)}{m} \right]$$

$$d = \sqrt[3]{\left[\frac{6 \cdot m_p}{\rho \cdot \pi} \right]}$$

Nombre de Ag NPs



Concentration et Flux

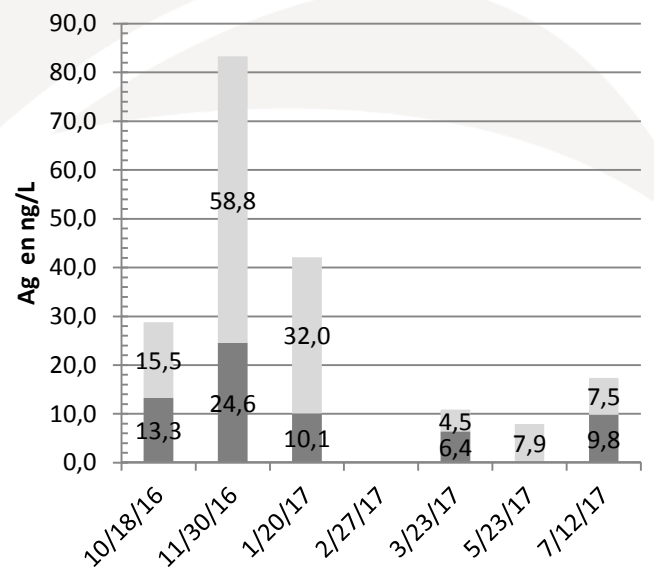
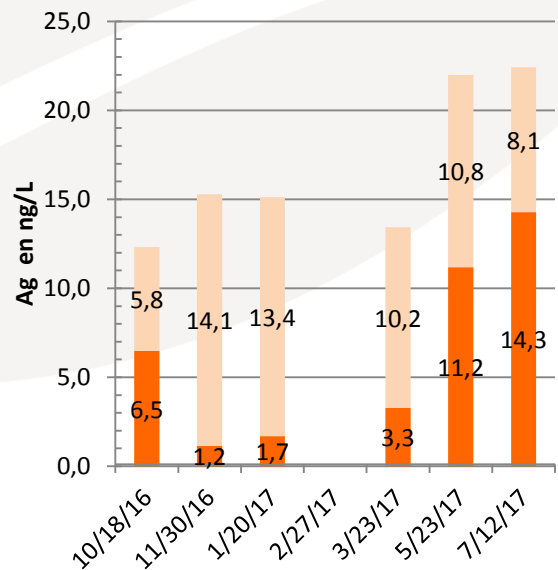
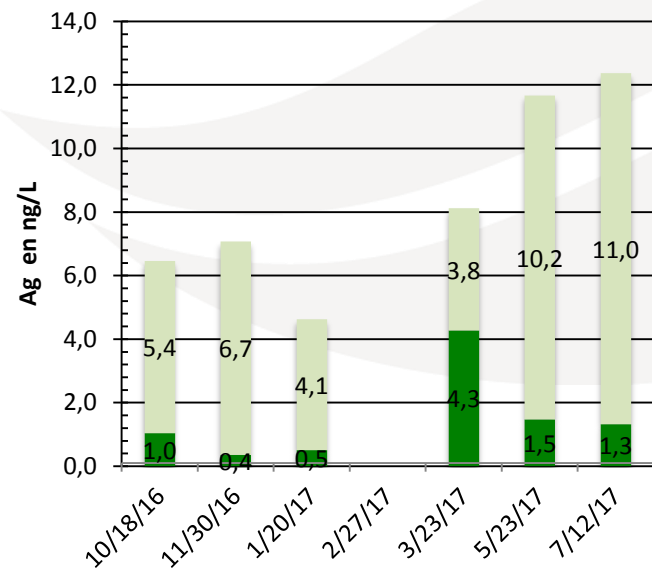
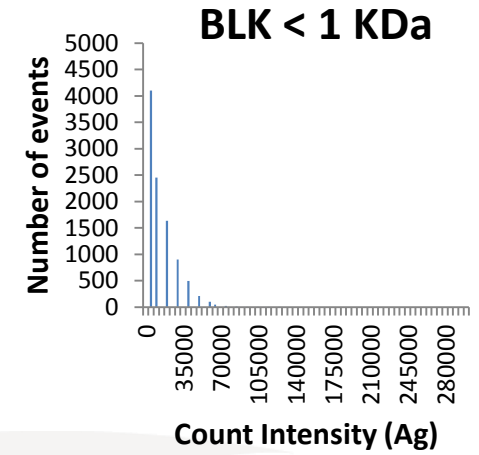


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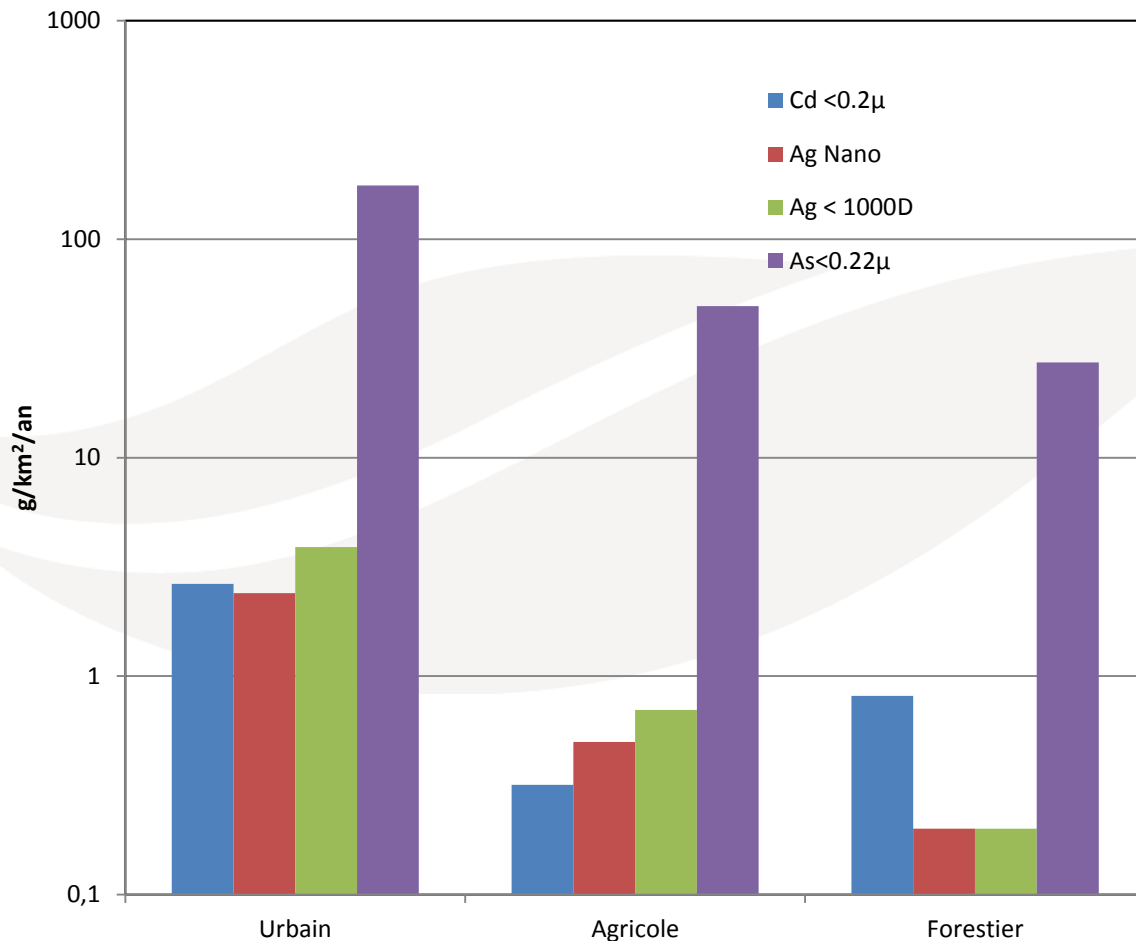
	ng/l
Urbain	11 ± 5
Agricole	8.4 ± 5
Forestier	1.5 ± 1.5

Dissous vs Nano

LQ = 50 ng/l sur échantillons filtrés 0.2µ



Ag vs Cd vs As



Environ Sci Pollut Res
DOI 10.1007/s11356-016-6981-0

RESEARCH ARTICLE

Trace metals dynamics under contrasted land uses: contribution of statistical, isotopic, and EXAFS approaches

Caroline A. Bannat¹, Alexander Göbber², Pascal Lévain¹, Guillaume Marin², Olivier Peron³, Marc F. Benedetti⁴

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Abstract Three sub-basins of the Seine River (France) under contrasted land uses (i.e., forested, agricultural, and urban) have been investigated in order to assess the origin and seasonal variation of trace metals, and evaluate their geochemical background and dynamics. Our results highlight a high anthropogenic impact on all elements for both the dissolved and particulate fractions. The main source for each element in the dissolved phase was determined and shows that transition and post-transition metals mostly originate from forested areas, while alkali and alkaline earth elements, cesium, lead, and halogens rather originate from agricultural land use. Conversely, for the particulate phase, most of the elements cannot be associated with a specific land use. Seasonal variation of elements was assessed according to the forested and agricultural land uses, and geochemical backgrounds were determined using average export rates, highlighting that the geochemical background for the forested land use is higher than the agricultural one for most of the elements. Finally, to

confirm these results, Zn dynamics in the three characteristic sub-basins and between the different land uses was investigated using a combination of Zn speciation, Zn isotopic ratio, and Zn export rates.

Keywords Land use · Trace metals · Sediments · Seine River · Zinc · Fluxes · Agriculture · Geochemical background

Introduction

Amongst trace metals contamination in aquatic environments has become a major issue following the important development of industrialization and urbanization. Trace metals released in the environment by anthropogenic activities can result in significant ecological and health issues due to their abundance and persistence in the environment, bioaccumulation, and toxicity (Vi et al. 2011; Zhu et al. 2015). Moreover, these anthropogenic inputs lead to a destabilization of natural biogeochemical cycles of elements, which can be at the origin of modification in trace metals dynamics. In order to protect water bodies, the European Union implemented the Water Framework Directive (Directive 2000/60/EC 2000) which commits its member states to achieve good qualitative and quantitative status in ecological and chemical fields of all water bodies by 2015. To do so, a list of 45 substances identified as priority pollutants for the European Union member states has been defined (Directive 2013/39/EU 2013), to which France added specific pollutants including silver, copper, chromium, and arsenic. However, the environmental quality standards given for these trace metals are provisional because they are not properly defined. Thus this perspective, the accurate determination of their geochemical background in natural systems is mandatory to define realistic pollution thresholds.

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Electronic supplementary material The online version of this article (doi:10.1007/s11356-016-6981-0) contains supplementary material, which is available to authorized users.

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Conclusions

Peut on détecter compter mesurer les NPs dans les rivières ?

Oui

Peut on déterminer l'origine des NPs ?

Pas encore

Peut il y a voir une effets du type d'usage des sols sur le type de NPs et leur flux?

Oui à confirmer avec les autres NPs : TiO_2 , CeO_2 et La_2O_3



Merci

Grazie

你好



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Dr. E. Alasonati



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Dr. I. Supiandi

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Dr. A. Gélabert