Environmental and industrial toxicology

PEGASE, AN INTEGRATED RIVER/BASIN MODEL DEDICATED TO SURFACE WATER QUALITY ASSESSMENT: APPLICATION TO COCAINE

J.-F. Deliege, E. Everbecq, P. Magermans, A. Grard, T. Bourouag, C. Blockx

Key words: Modeling, river quality, cocaine, micropollutants

ABSTRACT

The Aquapôle of the University of Liège has been involved in environmental modeling for more than 20 years. Among other, its current R&D unit focuses on the compartment of surface water, and – for modeling processes – is specialized on the water quality. One of its environmental models, called PEGASE (Planification Et Gestion de l'ASsainissement des Eaux), French acronym for "Planning and management of water purification" is devoted to the modeling of the environmental state of surface water, at different scales from small watersheds (10 km²) and basins up to entire transnational Districts (more than 100.000 km²). The software is used operationally by several administrations (Agencies and Ministries) mainly through Europe (France and Benelux, Germany ...), and several calculations have also been performed at international District levels for international commissions (Scheldt, Meuse, Moselle ...)

Recently, the PEGASE model has been adapted to describe the cocaine's behavior (using a stable metabolite of the cocaine in the environment: the benzoylecgonine) in waste water, waste water treatment plants (WWTP) and surface water. The cocaine is newly described in the model as an additional micropollutant (Pegase already treats numerous heavy metals), thanks to the implementation of new state variable equations and their specific parameterizations. At a first stage, only the urban sources (releases associated to the consumption by inhabitants) were considered as the industrial releases and the soil loads are assumed to be negligible. Simulations of benzoylecgonine have been done in the Walloon and Flemish regions, where many measurements from the COWAT project were available.

These first results are showing a good agreement between calculated and measured values. This ability of the model to simulate the fate of the cocaine derivatives in surface waters should be continued and extended to other metabolites.

Aquapôle,
University of Liège,
Sart Tilman Bâtiment B5,
Liège, Belgium

Address for Correspondence
Jean-François Deliege
Aquapôle, University of Liège
Allée des Chevreuils 3
Sart Tilman Bâtiment B53
4000 Liège
Belgium
Tel.: +32.4.3662356
Fax: +32.4.3665102
E-mail: jfdeliege@ulg.ac.be

INTRODUCTION

The Aquapôle of the University of Liège, Belgium, has been involved in environment modeling for more than 20 years. Its R&D unit focused on the development of models dedicated to surface waters, and specifically targeted to the simulation of the water quality. One of its environmental models, called PEGASE (Planification Et Gestion de l'ASsainissement des Eaux), French acronym for "Planning and management of water purification" is devoted to the characterization of the environmental state of surface water, at the scale of a whole watershed, basin and district (1). The software has been used operationally in several countries like France and Benelux, but several calculations have also been performed at international level for the international commissions in charge of the Scheldt and the Meuse.

Recently, a new, direct and objective way of monitoring drug consumption has been proposed, based on the measurement of urinary excreted drugs (and their metabolites) in waste and surface water (2, 3, 4, 5, 6, 7, 8, 9, 10).

In the COWAT study (10, 11, 12, 13, 14), quantification of cocaine (COC) and one of its metabolite (benzoylecgonine, BZE) in influent and effluent of waste water treatment plants and in surface water in Belgium were performed. The concentrations of COC and its metabolites were then converted into cocaine equivalents, using the flow rate of the water stream and a formula taking into account the molecular masses and the excretion pattern of cocaine and its metabolites. Finally, this study leaded to estimate the average consumption of cocaine per inhabitant.

These last results have allowed the development of a new application, which used the surface water quality PEGASE model to characterize the amount of cocaine in the rivers. The PEGASE module which already calculates the concentration of micro-pollutants (Cd, Cu, Zn, Pb, As, Ni, Cr, Ag, and Hg) has been completed with additional state variables and associated equations in order to represent the specific processes (adsorption, absorption, sedimentation, ...) taking place in surface waters for that kind of molecules. A key step is the calibration and the validation, which was realized by comparison between computed quantities and local measurements (from the COWAT project). The final objective was to run the model to obtain prospective scenarios at the scale of a whole watershed, helping authorities to assess the quantity of cocaine released in surface waters, and to control its spatial and temporal evolutions along the river, and/or through the year.

MATERIAL AND METHODS

The Pegase Model

The management of the aquatic resources is a particularly complex problematic, which involves many interrelated aspects. Decision making depends on competitive objectives and thus requires a multi-compartment, global-scale and synoptic approach. In this domain, an approach based on mathematical models is relevant and highly recommendable. E.g., the PEGASE model allows assessing the effects of some laying out policies, and provides the water decision-makers with a water system analysis tool for seeking alternative or more efficient solutions.

The purpose of the PEGASE model is to provide a tool to decision-makers – as regards to surface water management – which calculates the pressure-impact relations (i.e. the water quality according to pollutant contributions, releases and hydrological conditions).

The PEGASE model was built with the following motivations:

- better understanding of the aquatic environment mechanisms (hence the construction of a deterministic and physically based model which requires very few calibration to be applied to new basins);
- structure knowledge (including the "data input" through full relational databases);
- extend and complete the physical and chemical measurements network from discrete (spatially and temporally) points to the full unstationary river streams;
- describe and quantify the physically based "pressure – impact" relations and to help the authorities in charge of the surface water management in their process of decision making (future management plans);
- extend the river models to explicitly take into account the influence of their watershed.

PEGASE is an integrated model "basin/river" which makes possible to calculate in a deterministic way the water quality of rivers according to pollutant contributions and releases, for various stationary hydrological situations. Obviously, the model can also operate in non stationary mode over several years. It can also provide an estimated calculation of the water quality improvements resulting from purification actions or release reductions. The model includes hydrological and hydrodynamic sub-models, a thermal sub-model, a sub-model dedicated to releases, and a sub-model dedicated to calculate the water quality and to explicitly describe the aquatic ecosystem mechanisms.

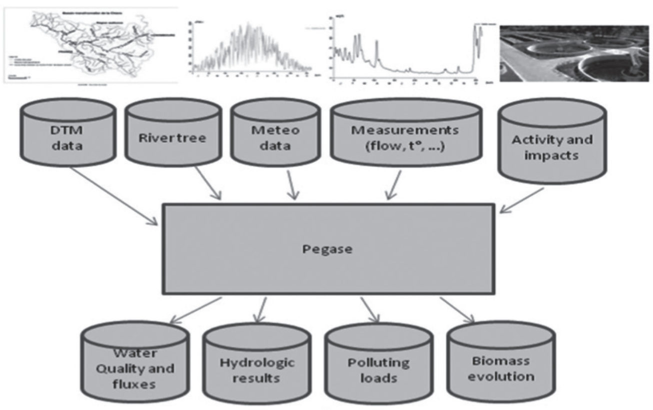

Figure 1 *— PEGASE data flow*

PEGASE was initially developed for the Walloon Region (at the end of the eighties). It was then adapted, improved and applied to other river basins. A special attention is paid by the developers to

(1) the upgrading possibilities (continuous improvement),
(2) the programs' modularity, and
(3) the needs of and the feedbacks from the end-users (existence of a user community).

The relevant utility of the PEGASE model was further increased in the 2000th with the setting up of the European Directive 2000/60/CE establishing a framework for Community action in the field of water policy. Currently, PEGASE is used in the Walloon Region, but also in France (by four water agencies), in the Flemish Region, in the Luxembourg and for several international basins (the Meuse, the Scheldt, the Mosel-Saar). Some applications were also tested on the upper Wisla River (Poland), the Nicolet River (Canada) or the river basin of Itajai (Brazil).

PEGASE simulates classical macro-pollutants (DO, BOD, COD, N, P), but also micro-pollutants (mainly heavy metals).

PEGASE model is fed by several kinds of inputs:

- **Geographical data:** the PEGASE model uses digitalized water courses, hydrological contours, digital terrain models, land cover, livestock, administrative reference frame;
- **Hydro-meteorological data:** PEGASE uses measurements of daily water flows, daily temperatures, and insolation;
- **Data related to human activities and releases** (industrial, urban, waste water treatment plants, ...): PEGASE describes in a structured way the urban releases, the industrial releases, the role of the purification plants, the releases due to livestock farming activities, and the diffuse contributions by the soils:
  - urban releases are estimated based on the concept of "inhabitant equivalents" : the flux of pollution emitted per day per capita;
  - industrial releases are estimated by administrative statistics (tax data, ...).

The input data can be processed and visualised using Geographical Information System (GIS).

THE COWAT STUDY

A new approach for estimating cocaine consumption, based on the analysis of cocaine (COC) and its metabolites benzoylecgonine (BZE) and ecgonine methyl ester (EME) in water samples has been applied in 2007 and 2008 to 28 rivers and 41 waste water treatment plants in Belgium. This study, (the COWAT project — COcaine in WATer) has been carried out using solid-phase extraction and liquid chromatography coupled to tandem mass spectrometry. While EME was undetectable, COC and BZE were detectable with concentrations ranging from <1 to 753 ng/l and <1 to 2258 ng/l, respectively. BZE concentrations were employed to calculate the local amount of abused cocaine. The highest values (up to 1.8 g/day cocaine per 1000 inhabitants) were found in large cities and during weekends. The estimation of cocaine abuse through water analysis can be realized on regular basis without cooperation of consumers. It also gives clear geographical information, useful to prevention campaigns which can be more easily organized, implemented and evaluated.

PEGASE and cocaine

The Pegase model has been used to simulate the cocaine fate in the Belgian surface waters. As more or less 45% of the cocaine is metabolized in benzoylecgonine (BZE) and as BZE is quite stable in the aquatic environment, it is a good candidate to be modeled (as a state variable). Then, test simulations were not done on the cocaine itself, but on one of its metabolites: the benzoylecgonine.

The BZE has been represented in the PEGASE model as a micropollutant, with specific parameterization.

Concerning the releases of BZE, only urban releases (consumption by inhabitants) were considered: industrial releases and soil loads were assumed to be negligible.

The characterization (parameterization) of a new micro-pollutant is a very important task taking place at the beginning of the new application to a domain.

The main parameters needed for modeling the BZE were:

- the urban releases (a inhabitant equivalent (IE), mg/IE.day);
- the rate of adsorption/desorption upon particles in suspension;
- the rate of degradation in surface waters;
- the rate of reduction in WWTP.

In this test application, an estimation of these parameters has been made on the bases of the following assumptions:

- urban releases : the urban releases were estimated using the inhabitant equivalent (like classical pollutants). Simulations were made with a constant value of 0.15 mg BZE/IE.day, corresponding to the median value measured in the COWAT study;
- WWTP : the rate of reduction of BZE in WWTP - were taken at 95% (mean value measured in the COWAT study);
- rate of degradation : the BZE has been supposed non degradable;
- adsorption/desorption processes on suspended matter have been parameterized with "typical values" used for other micropollutants.

In the modeling processes, the waste system (from releases to waste water treatment plants [trough sewer] and then to the rivers) is completely described. The purification processes are also modeled and all potential transfers between compartments are taken into account (direct discharges to the rivers, losses from sewer system, industrial treatment plants ...).

RESULTS

Simulations were made for the year 2007, in the Scheldt basin[1] and in the Walloon region[2].

Non stationary simulations were made from 1st January to 31th December 2007. For validation, computed concentrations (mean daily values) were compared to the values measured at the same place and date in the COWAT study.

A first partial validation has been done on the releases data: BZE fluxes computed by the Pegase release submodel (based on the equivalent inhabitant concept) have been compared with the punctual measured fluxes at the entry of WWTP. **Figure 2** shows this comparison:

- On the X axis are plotted the computed values at the entry of the treated WWTPs, based on a daily equivalent inhabitant of 0.150 mg BZE/IE.day;
- On the Y axis are plotted the measured values at the entry of the treated WWTPs.

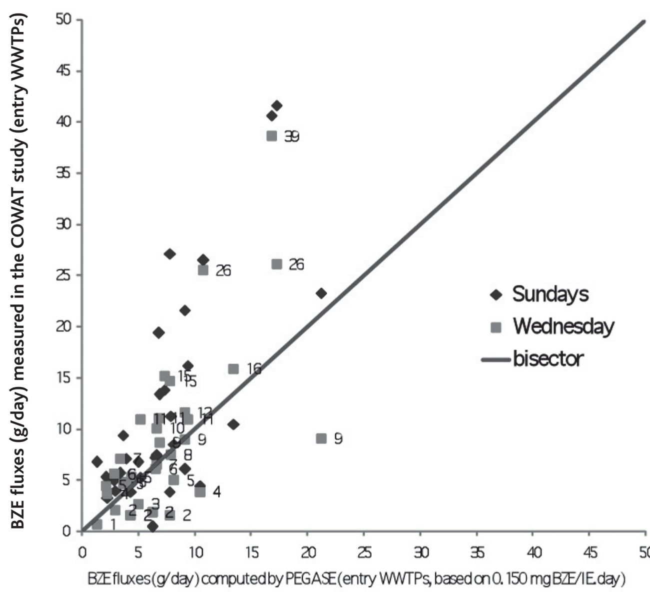

Figure 2 — *Comparison of BZE fluxes in the entry of WWTP*

It can be seen that there is a good agreement for small sewage treatment plants. For larger stations, the fluxes calculated by Pegase seem to be underestimated with respect to the fluxes measured at the entry of the same WWTPs in the COWAT study. This can be explained by the use in the simulations of a constant equivalent inhabitant (in fact, consumption of cocaine should be higher in large cities).

Pegase computes, for every day of the year, the average concentrations on the whole explicitly described river network each 50 meters. The results associated to a Pegase simulation represent a huge amount of information and graphics.

The main results of the first cocaine simulation of the surface water quality model are produced here af-

---

[1] *A PEGASE application is made for the Vlaamse Milieu Maatschappij (Flemish Water Agency) on the Belgian Scheldt basin*

[2] *PEGASE is also applied for the entire Walloon region (mainly the Belgian Meuse basin)*

ter as water quality profiles along rivers and temporal evolutions (presented at some rivers spots).

The validation task of the simulation is based on a comparison between the calculated values (solid lines) and the measured values (dots) of BZE at points where COWAT measurements were available.

Figure 3 shows computed and measured BZE concentrations (ng/l) in the Dijle River (at the location of km 38 from the source of the river, at the city of Limelette) for the year 2007:

- solid blue line: computed total concentrations of BZE;
- dotted green line: computed dissolved concentrations;
- dotted brown line: computed concentrations of adsorbed BZE on suspended matter;
- red point: measured value (from the COWAT study).

We can see here that there is a good agreement between the (only one) measured value and the simulated values.

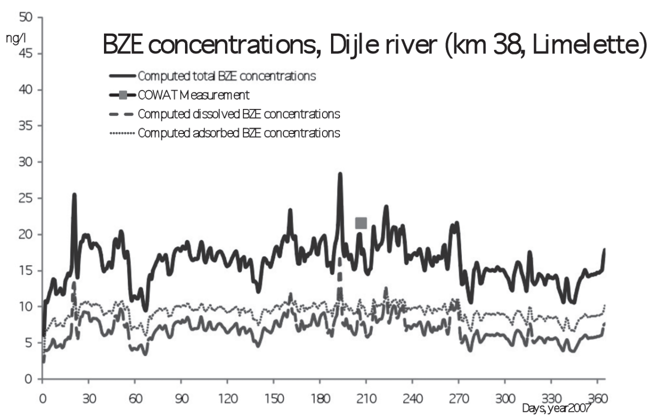

Figure 3: Annual evolution of the BZE concentrations (ng/l) on the Dijle River – km 37.9, year 2007

Figure 4 shows the results for the Zenne River, downstream the town of Brussels (which was not yet completely purified). We can see here:

- that the computed and measured concentrations of BZE are much higher (300-500 ng/l) that in the Dijle River (20-30 ng/l);
- that the computed values underestimate slightly the measured value; this can be explained by the underestimation of the inhabitant equivalent in the large cities (see above).

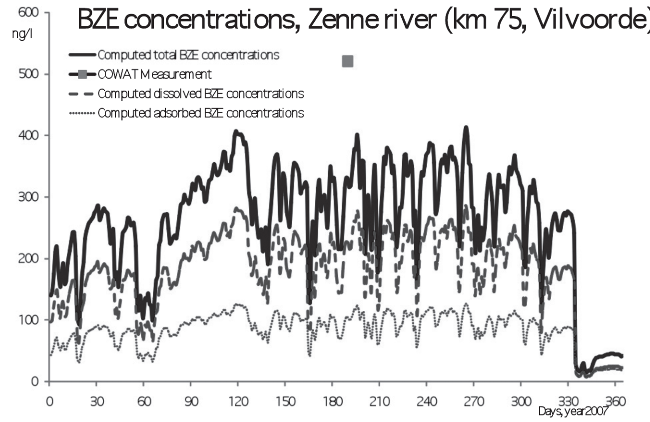

Figure 4: Annual evolution of the BZE concentrations (ng/l) on the Zenne River – km 40, year 2007

Another way to present the results is to show longitudinal profiles, along the rivers (from its source to its confluence), of the computed values for a specific day, with the measurements acquired for the same day.

Figure 5 shows this kind of graphic for the Dijle River on the 17th July 2007. We can see a good agreement between computed and measured values (although there is a small underestimation of the computed values).

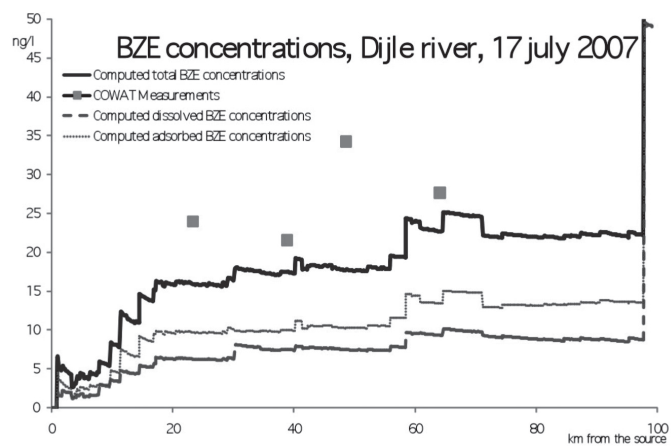

Figure 5: Longitudinal profile of the BZE concentrations (ng/l) on the Dijle River, the 17th of July 2007

Figure 6 shows the same type of result for the Aa River. We can see, here, one of the main advantages of the methodology: the model highlights areas where high concentrations can be simulated, even if no measurements exist and if existing measurements tend to expect lower values.

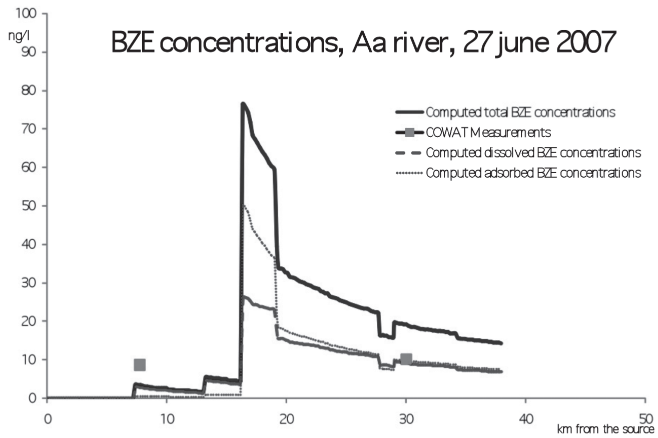

Figure 6: *Longitudinal profile of the BZE concentrations (ng/l) on the Aa River, the 27th of June 2007*

Figure 7 shows a map with calculated concentrations on the whole hydrographic network simulated by the PEGASE model. This kind of graphic allows having a global synoptic view of the concentrations of BZE in all the river system.

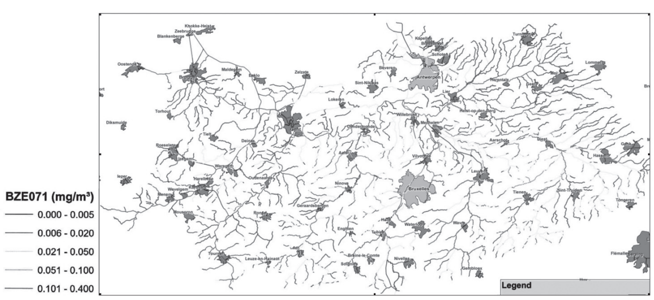

Figure 7: *Simulated BZE concentrations (ng/l) in the Belgian Scheldt basin, the 27th of June 2007*

Calibrating and validating a model like PEGASE on a new basin (domain) can take several months (or years), because validation not only concerns the model itself, but also and primarily the data (flows, releases ...). We can then conclude that, for a first application on the cocaine metabolite BZE, with a first new set of input data (especially releases) and with a very short calibration/validation period, the results are very encouraging.

DISCUSSION

This test study has shown:

- the ability to simulate with the PEGASE model the fate of the cocaine metabolite in surface waters;
- the consistency of cocaine and its metabolite measurements made in the framework of the COWAT study;
- the ability to estimate through measurements in rivers and use of modeling, the consumption of cocaine (and its evolution in time and space).

A better knowledge of cocaine sources could be obtained using the model in reverse mode. To do so, the following improvements should be undertaken:

- use of a PEGASE population equivalent "variable" in space (large cities) and time (week-end consumption, ...);
- use of better data (numerous measurements spots and frequencies) for calibration / validation.

An extension of the model to other metabolites (drug residues, pharmaceuticals as endocrine-disrupting contaminants ...) is also possible in the coming years.

Acknowledgements*:* the Aquapôle thanks the SPW (Public Service of Wallonia, Belgium) and the VMM (Vlaamse Milieumaatschappij, Belgium) for their permission to use their data in the context of this study.

REFERENCES

1. Deliege JF, Everbecq E, Magermans P, Grard A, Bourouag T, Blockx C. Pegase : a software dedicated to surface water quality assessment and to European database reporting. *Proceedings of the European conference of the Czech Presidency of the Council of the EU TOWARDS eENVIRONMENT. Opportunities of SEIS and SISE: Integrating Environmental Knowledge in Europe. Masaryk University, Brno, Czech Republic*, March 2009, 24-31.
2. Bones J, Thomas KV, Paull B. Using environmental analytical data to estimate levels of community consumption of illicit drugs and abused pharmaceuticals. *J Environ Monitoring* 2007; 9: 701–707.
3. Castiglioni S, Zuccato E, Crisci E, Chiabrando C, Fanelli R, Bagnati R. Identification and measurement of illicit drugs and their metabolites in urban wastewater by liquid chromatography–tandem mass spectrometry. *Anal Chem* 2006; 78: 8421–8429.
4. Gheorghe A, van Nuijs A, Pecceu B, et al.Analysis of cocaine and its principal metabolites in waste and surface water using solid-phase extraction and liquid chromatography–ion trap tandem mass spectrometry. *Anal Bioanal Chem* 2008; 391: 1309–1319.
5. Huerta-Fontela M, Galceran MT, Ventura F. Ultraperformance liquid chromatography–tandem mass spectrometry analysis of stimulatory drugs of abuse in wastewater and surface waters. *Anal Chem* 2007; 79 : 3821–3829.

5. Hummel D, Löffler D, Fink D, Ternes TA. Simultaneous determination of psychoactive drugs and their metabolites in aqueous matrices by liquid chromatography mass spectrometry. *Environ Sci Tech* 2006; 40 : 7321–7328.
6. Kasprzyk-Hordern B, Dinsdale RM, Guwy AJ. Multiresidue methods for the analysis of pharmaceuticals, personal care products and illicit drugs in surface water and wastewater by solid-phase extraction and ultra performance liquid chromatography–electrospray tandem mass spectrometry. *Anal Bioanal Chem* 2008; 391 : 1293–1308.
7. Zuccato E, Castiglioni S, Bagnati R, Chiabrando C, Grassi P, Fanelli R. Illicit drugs, a novel group of environmental contaminants. *Water Research* 2008; 42: 961–968.
8. Zuccato E, Chiabrando C, Castiglioni S., et al. Cocaine in surface waters: a new evidence-based tool to monitor community drug abuse. *Environmental Health: A Global Access Science Source* 2005; 4 : 14–20.
9. Van Nuijs ALN, Pecceu B, Theunis L, et al. Cocaine and metabolites in waste and surface water across Belgium. *Environ Pol* 2009; 157: 123-129
10. Theunis L, van Nuijs A, Pecceu B et al. Cocaïne dans nos rivières : une approche méthodologique originale dans le domaine de la toxicologie environnementale. *Revue Médicale de Liège* 2008 ; 6 : 39-43.
11. Van Nuijs A, Pecceu B, Theunis L, et al. Spatial and temporal variations in the occurrence of cocaine and benzoylecgonine in waste- and surface water from Belgium and removal during wastewater treatment. *Water Research* 2009; 43: 1341-1349.
12. Van Nuijs A, Pecceu B, Theunis L, et al. Can cocaine use be evaluated through analysis of wastewater? A nationwide approach conducted in Belgium. Addiction 2009; 104: 734-741.
13. Van Nuijs A, Pecceu B, Theunis L, et al. Can cocaine use be evaluated by analysis of waste water? An original nationwide approach. Lancet 2009 in press.