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Population mobility and urban wastewater dynamics

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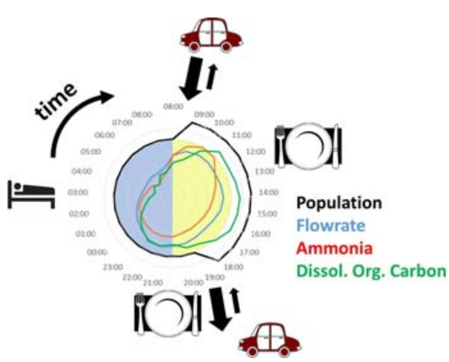
HIGHLIGHTS

- Daily commuters can increase the effective number of domestic pollution producers.
- Census data help to understand the domestic pollution production in a catchment.
- pH and conductivity may not exhibit clear diurnal variations.

GRAPHICAL ABSTRACT



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ABSTRACT

Dynamic influent models, which have been proposed to test control strategies using virtual wastewater treatment plants, should be as realistic as possible. The number of inhabitants in the catchment at any given time and their ways of life are among the parameters affecting the quality of these models. Census data related to work and school commutes were used to evaluate the number of people present in a given urban area. Based on the example of a large urban catchment (Grand Nancy, France), the results show that a population increase of 30% could occur during working hours resulting from the imbalance between workers leaving and coming into the catchment. Combined with information related to the local way of life, variation in the population helps to explain changes in wastewater flow rate and pollution (carbon, nitrogen, phosphorus and heavy metals), which present several maxima reflecting daily activities, such as bladder voiding, meals, the use of washrooms, etc. However, no well-defined variation patterns for pH and conductivity, which are linked to the concentrations of anions and cations in the wastewater, were observed. Slight reductions (up to 10% on Sundays) in the flow and pollution load were observed on weekends as the commuter flow decreased. Census data proved to be efficient in helping to understand the daily pattern of urban wastewater characteristics.

1. Introduction

Wastewater treatment plants (WWTP) are subject to large disturbances related to variations in the flow and composition of the incoming

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wastewater; such variations are due to human activity in the catchment or rainfall in the case of combined sewage systems. These disturbances should be addressed using an appropriate control strategy to ensure the quality of the treated water with respect to the regulations. Biological wastewater treatment with activated sludge is commonly used around the world, especially in large wastewater catchments. In this process, the control of aeration is particularly demanding: its optimization is linked to the minimization of the energy used in a plant. Currently, the issue of greenhouse gas production (carbon dioxide and nitrous oxide) should also be considered, and a clear connection has been made between aeration and the emission of these gases (Leix et al., 2017; Massara et al., 2017). Because tests of new control strategies using real WWTPs are not practical, full-scale plant dynamic models (virtual WWTPs) have been developed (Butler and Schütze, 2005; Nopens et al., 2010) and used for various purposes. For example, Fernández-Arévalo et al. (2017) described how such models can be used to quantitatively assess energy costs and recovery in WWTPs. The success of this approach is dependent upon the realism of the simulated variations in the wastewater characteristics (flow rate and composition) used to create disturbances at the inlet of the virtual WWTP.

It is recognized that the chemical and bacteriological composition of wastewater varies greatly according to wastewater origin. Such variation is a function of dietary habits, lifestyle, habitat (urban or rural), population density, socio-economic factors, climatic conditions and flow conditions in sewage systems (Butler and Gatt, 1996; Eriksson et al., 2002; Sperling, 2007; Henze and Comeau, 2008; Rodier et al., 2016). Rainfall events affect also wastewater composition because, in combined sewers, these events lead to increases in flow and in the contribution of pollutants, stored in sewer sediments and/or deposited on impervious surfaces, which are washed out (Gasperi et al., 2010, 2012).

Urban wastewater composition surveys are generally conducted on the basis of classical pollution parameters (i.e., in terms of chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), total nitrogen (TN), etc.) at the inlet of WWTPs as well as at source points: bathrooms, toilets, laundry facilities (washing machines), and kitchens (including dishwashers) (Butler et al., 1995; Gromaire-Mertz et al., 1998; Eriksson et al., 2003; Kafi et al., 2008). More recently, studies have focused on identifying the urban sources of micropollutants (metals, pesticides, pharmaceuticals, etc.) or assessing their contributions to water quality degradation (Donner et al., 2010; Plósz et al., 2010; Salgado et al., 2011; Choubert et al., 2011; Gasperi et al., 2014; Deshayes et al., 2015). Toilets produce the most important loads of nitrogen, phosphorus and suspended solids (Gray and Becker, 2002). They represent 60 to 90% of the total flow at the end of the night or early morning and 20–40% during the day. Data on relatively common inorganic species, such as calcium, magnesium, etc., or on anions, such as sulfates or chlorides, are rare (El Khatib et al., 2012; Thitanuwat et al., 2016), although there is growing interest in these species in terms of either resource recovery (such as magnesium for struvite) or pH modelling in sewers (Sharma et al., 2013) and during wastewater treatment (Flores-Alsina et al., 2015; Mbamba et al., 2015; Solon et al., 2015).

Depending on the scale of observation and analysis, daily, weekly, seasonal and annual variability occurs. Some studies include the daily variability in wastewater characteristics (flow rate and BOD in Matos et al., 2013, flow rate and temperature in Cippola and Maglionico (2014a), COD, TOC and ammonia in Eriksson et al. (2009), biocides in Bollmann et al. (2014), PFOS and PFOA in Pasquini et al. (2011), surfactants in Camacho-Muñoz et al. (2014), ibuprofen, sucralose, ofloxacin and 4-nonyphenol in Pasquini et al. (2014)). Socio-demographic characteristics affect the daily cycles of water use (Matos et al., 2013) and therefore those of wastewater. In an urban context, the highest values of COD, TSS, BOD, etc. are usually measured during diurnal hours, with a peak in the morning (more pronounced) and several peaks in the early evening (more distributed) (Sperling, 2007). This behavior is in agreement with the pattern of water consumption in urban areas, which is higher during the same period (Camacho-Muñoz et al., 2014). The sewage flow rate and temperature monitored by Cippola and Maglionico (2014a) for long periods of time reveal three peaks during the day and a large minimum at night. The flow values at each measuring point depend on the number of inhabitants in the catchment drained by the sewer system (Cippola and Maglionico, 2014b). Larger sewer networks have more consistent diurnal flow rates and lower variation in concentration (Gernaey et al., 2011), although morning and evening peaks are still visible in the pollution data of Bogota, a megacity of 8 million inhabitants (Rodriguez et al., 2013).

If the improvement of WWTP performance relies on knowledge regarding variation in the flow and composition of wastewater, large-scale measurement campaigns require a heavy workload, are expensive and cannot be carried out for extended periods of time. Therefore, models have been proposed to create synthetic wastewater files to be used in long-term simulations. They can be deterministic (Zug et al., 1999; Schütze et al., 2002; Vanrolleghem et al., 2005), mixed with a certain proportion of stochasticity to take into account uncertainty regarding influencing factors (Gernaey et al., 2011) or fully probabilistic (Talebizadeh et al., 2016). The phenomenological model proposed by Gernaey et al. (2011) and used in subsequent works by Rodriguez et al. (2013), Flores-Alsina et al. (2014) and Saagi et al. (2016) was very simply constructed, with a limited number of parameters that have physical meaning but maintain a high degree of flexibility to enable adaptation to different catchment configurations. The model is divided into four main blocks to describe the wastewater flow rate, pollutants (carbon, nitrogen and phosphorus) and temperature and the transport of water and pollutants in the sewer. The two first blocks are further subdivided into domestic and industrial cases. The proposed basic flow rate and daily pollutant profiles are based on travel to and from work for the residents, but whether all the residents are working or whether they work in the catchment are not specified. These basic profiles were subsequently used by Saagi et al. (2016, 2017). No details on the assumed daily profiles are given by Flores-Alsina et al. (2014) in their validation of the model with full-scale data obtained from two large Scandinavian WWTPs.

To obtain good estimates of wastewater characteristics with respect to time goes beyond their simple use in simulation models. The models are also used to analyze the consumption of licit and illicit drugs. Coutu et al. (2016) proposed an integrated stochastic model for pharmaceuticals, taking into account their ingestion and excretion by humans and their degradation and transport in the sewers. Snip et al. (2014) added a pharmaceutical-dedicated module to the initial Gernaey et al. (2011). The model works reasonably well, but discrepancies in the estimated and observed micropollutant loads can be observed at midday for some substances (Snip et al., 2016). Such discrepancies could be due to uncertainties concerning the number of persons present in the catchment during the day.

Daughton (2012) proposed the use of human biomarkers, such as creatinine (in urine) or coprostanol (in feces), to obtain a real-time estimate of the population present in an area. Pharmaceutical and personal care products as well as licit/illicit drugs (Brewer et al., 2012; O'Brien et al., 2014; Lai et al., 2015; Gao et al., 2016; Rico et al., 2017) have also been tested for such back-calculation, but all these molecules require complex analytical tools, and their analysis is expensive. Very recently Thomas et al. (2017) have proposed the use of data collected from mobile devices (such as cell-phones) to quantify the variability of the people presence in a catchment. This could lead to very detailed variability data in the future but has not been deployed to a very large scale.

Our objective is to relate the variation in wastewater flow rate and pollution in an urban catchment to the daily mobility of the population as assessed from surveys by census authorities.

2. Materials and methods

For illustrative purposes, French national population survey databases were used to assess the fluxes of people commuting to work or to school daily in and out a large urban catchment. The collected information facilitates discussion of the wastewater flow rate and pollution dynamics obtained through several sampling campaigns.

2.1. Description of the catchment

The catchment under evaluation is located in northeastern France (Grand Est region) and covers approximately 192 km^2. It is composed of the 20 municipalities of the "Grand Nancy" Metropolis (Art-sur-Meurthe (#1), Dommartemont (#2), Essey-les-Nancy (#3), Fléville-devant-Nancy (#4), Heillecourt (#5), Houdemont (#6), Jarville-la-Malgrange (#7), Laneuveville-devant-Nancy (#8), Laxou (#9), Ludres (#10), Malzéville (#11), Maxéville (#12), Nancy (#13), Pulnoy # (14), Saint-Max (#15), Seichamps (#16), Saulxures-les-Nancy (#17), Tomblaine (#18), Vandœuvre-les-Nancy (#19), and Villers-les-Nancy (#20)) (approximately 254,000 inhabitants in an area of 142 km^2) and the municipalities of Champigneulles (C) (6920 inhabitants; 24 km^2), Frouard (F) (6800 inhabitants; 13 km^2), Messein (M) (1900 inhabitants; 5 km^2) and Pompey (P) (4870 inhabitants; 8,1 km^2) (Figure SI1 in Supporting Information). Nancy (with 104,500 inhabitants) and Vandoeuvre-les-Nancy (with 30,000 inhabitants) are the largest municipalities in the catchment (Figure SI2 in Supplementary Materials). The wastewater is directed to the Maxéville WWTP through a sewer system. The sewerage network is 50% unitary. In total, approximately 275,000 persons equivalent are connected to the WWTP.

The economy of Grand Nancy is essentially tertiary. This sector contains 87% of the jobs. More than half of the commercial activity of the agglomeration is concentrated in the municipality of Nancy (more than 70% of the personal goods stores, nearly 40% of the hotels and restaurants and 40% of the home equipment stores). Grand Nancy is also the first hub of higher education in the Lorraine region. The largest part of the University is contained in the municipalities of Nancy and Vandoeuvre-les-Nancy.

2.2. Sampling campaigns

Eleven sampling campaigns were carried out at the inlet of the Maxéville WWTP between 2009 and 2016 (Table SI1 in Supporting Information). Samples were collected under dry weather conditions every hour over 24-hour periods on different dates using an ISCO 3700 autosampler (Ponsel Mesure, Caudan, France). The samples were stored at 4 °C in polyethylene bottles for transport to the laboratory, where they were analyzed within 24 h. The wastewater flowrate was measured by means of an electromagnetic flowmeter (Proline Promag 50P from Endress + Hauser, Huningue, France).

Conductivity, pH, turbidity, chemical oxygen demand (COD), dissolved organic carbon (DOC), major anions (nitrates, nitrites, sulfates, chlorides and o-phosphates) and cations (ammonium, sodium, potassium, calcium and magnesium) and some metals (Table SI2 in Supporting Information) were measured. The analytical methods used were based on the principles of the NF-EN-ISO standards while observing the requested quality assurance/quality control rules.

2.3. Databases

The INSEE (National Institute for Statistics and Economic Studies) (http://www.insee.fr) provides two large databases related to population travel from home to work places (FD_MOBPRO) and from home to study places (FD_MOBSCO). The FD_MOBSCO covers individuals between 2 and 35 years old. A FORTRAN software was specifically developed to extract the relevant information from these databases, i.e., for each community, how many persons are working in the community, how many are commuting to work in another community, and how many are commuting from another community to work there. The same procedure was applied to study school enrollment. Data mining focused on the 2010–2013 period.

Monthly and yearly information related to drinking water production and wastewater treatment was collected from the annual activity reports of Grand Nancy (http://www.grandnancy.eu) on the quality of the water and wastewater services.

Data on the daily averages of urban wastewater flow and pollution parameters at the inlet of the Maxéville treatment plant were also collected for 2009 to 2014 from the Rhin-Meuse Water Information System (http://rhin-meuse.eaufrance.fr). To distinguish between dry and rainy days, daily rainfall data were collected from the Meteo-Ciel website (http://www.meteociel.fr/) for the Nancy-Essey weather station. Historical averages for the same station were obtained from InfoClimat (http://www.infoclimat.fr/).

2.4. Data processing

Hourly averages of the flow and pollution parameters were calculated for all sampling campaigns. The minima, maxima, means, standard deviations, variation coefficients, medians and 1st and 3rd quartiles were computed for daily flow and pollution parameters. Using the values obtained, it was possible to identify possible correlations between ammonium concentration (used as an anthropogenic pollution indicator) and the other parameters to assess their links with human pollution. Student's *t*-test was used to assess the statistical significance of the correlations at 5%. The different calculations and graphical representations were conducted using Microsoft Excel.

3. Results and discussion

3.1. Population mobility

Fig. 1 shows the number of individuals travelling for work within the catchment during weekdays (Monday to Friday), as well as those coming from outside the catchment or travelling out of the catchment (approximately 19,500 individuals, among which 42% have their home in Nancy (#13) – block A in Fig. 1). Nancy also attracts many workers from within the catchment, as 26% of the working residents work in Nancy (block B in Fig. 1). Nancy is also the municipality that attracts the most workers from outside the catchment (i.e., ≈42,500 individuals or 40% of the incoming work force – block C in Fig. 1). Vandoeuvre-les-Nancy attracts 15% of the incoming work force (block D in Fig. 1). The largest part of the work force commutes every day.

A similar analysis can be conducted for travel related to education (Figure SI3 in Supporting Information). The catchment contains approximately 79,500 schoolers and higher-education students. The percentage of daily commuters is unknown, but 64% of the concerned individuals are older than 18 years. Approximately 70% of the education-related commuters are enrolled in Nancy (#13, 61% - block F) and Vandoeuvre-les-Nancy (#19, 9% - block H). They are likely to be enrolled in higher-education institutions and to commute on a weekly or even longer basis. Approximately 50% of education-related individuals registered in the catchment are enrolled either in Nancy (40% - block E) or Vandoeuvre-les-Nancy (10% - block G).

Globally, the catchment has approximately 195,000 active residents, with 58% workers and 42% schoolers and higher-education students. Of these residents, 88% stay in the catchment all day. In addition to them, approximately 150,000 individuals come to work and school in the catchment. Approximately 362,000 individuals can be present in the catchment during the day, compared to the municipal population of 274,000 individuals present at night and during weekends.

The expected increase in daily population with respect to the municipal population greatly varies in the catchment depending upon the community, as shown in Figure SI4 (Supporting Information). Nancy and Vandoeuvre-les-Nancy have an expected daily population increase of 33% and 47%, respectively. The largest increases were observed for Ludres (#10), Houdemont (#6) and Fléville-devant-Nancy (#4), at 85%, 71% and 65%, respectively. These municipalities have large

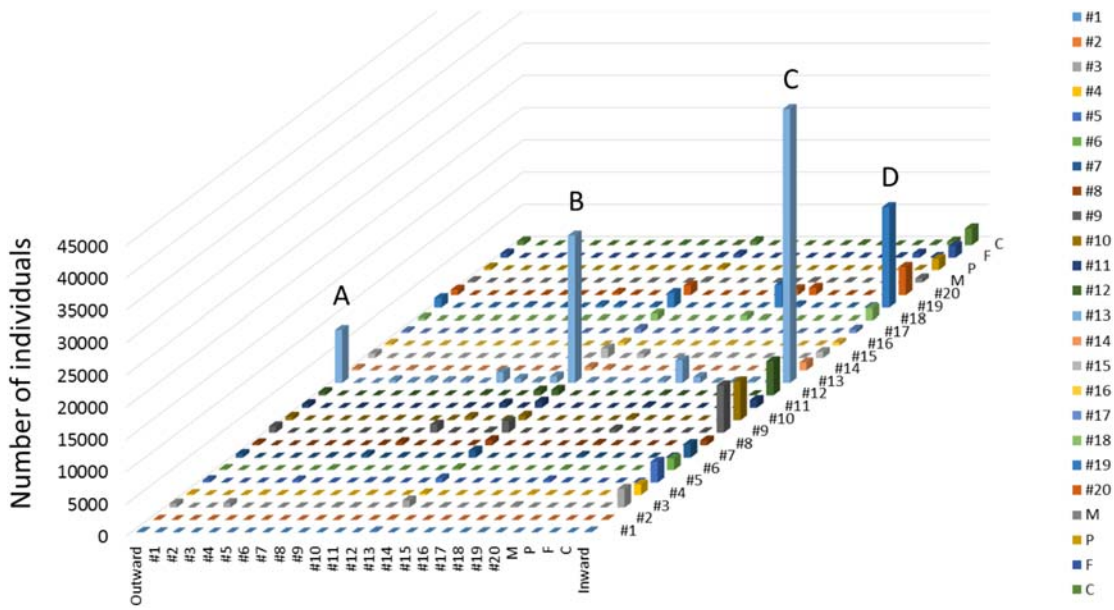

Fig. 1. Home-work travel. Codes for municipalities: Art-sur-Meurthe (#1), Dommartemont (#2), Essey-les-Nancy (#3), Fléville-devant-Nancy (#4), Heillecourt (#5), Houdemont (#6), Jarville-la-Malgrange (#7), Laneuveville-devant-Nancy (#8), Laxou (#9), Ludres (#10), Malzéville (#11), Maxéville (#12), Nancy (#13), Pulnoy # (14), Saint-Max (#15), Seichamps (#16), Saulxures-les-Nancy (#17), Tomblaine (#18), Vandœuvre-les-Nancy (#19), Villers-les-Nancy (#20), Champigneulles (C), Frouard (F), Messein (M) and Pompey (P).

industrial and commercial areas with shopping centers, which explains the presence of commuting workers with respect to the municipal population of the concerned municipalities. The average drinking water volume, calculated as the ratio of the total distributed drinking water volume to the municipal population of the catchment, is 148 L/inh. The highest drinking water volumes were observed for Ludres (223 L/inh) and Houdemont (211 L/inh), in agreement with the daily population increase.

The analysis of the travel of the population to work and school has revealed that for a large urban catchment, it is likely that there is an increase in population during the day and not a decrease, as has been generally assumed in the literature (Gernaey et al., 2011; Flores-Alsina et al., 2015). Similar findings have been obtained for twenty large US cities with at least 500,000 residents, where the daily population change was varying between 10% and 78% (Laughlin et al., 2015).

3.2. Wastewater dynamics

The wastewater dynamics recorded at the inlet of a WWTP are the result of the combination of production at a source (households, industry) and transport along the sewer network. Table SI3 (Supporting Information) presents the characteristic values of the wastewater flow rate and physico-chemical parameters at the inlet of the Maxéville WWTP obtained during the sampling campaigns.

Fig. 2a presents the variation in the average daily flow observed during the sampling campaigns. The error bars ($\pm\sigma$, where $\sigma =$ standard deviation) show the range of the variation in the daily flow for each hour. The weekday flow varies from 2500 to 4310 m^3/h, with an average of 3660 $\pm$ 660 m^3/h. The daily flow rate is 87,750 m^3/day. The close examination of the variation reveals the presence of three peaks, which appear at approximately 10:00 am, 2:00 pm and 9:00 pm. The 10:00 am peak comes from morning water consumption by residents who are getting prepared to go to work or school between 8:00 am and 9:00 am. The delay is due to the distance to the WWTP, the largest distance being approximately 15 km. The 2:00 pm peak is due to water consumption related to the lunch break, which lasts between 30 min to 2 h. The 9:00 pm peak is related to water consumption during evening activities (dinner, toilet, bathing, washing, cleaning, etc.). Dinner usually occurs between 7 pm and 9 pm in France. During the day, small decreases in flow rate are observed between 10:00 am and 2:00 pm and between 2:00 pm and 5:00 pm, at the peak of the working hours. From 9:00 pm to 6:00 am, there is a decrease in flow, reflecting the sleeping period, with low water consumption. The time and origin of peaks are in agreement with the findings of other authors, such as Cippola and Maglionico (2014a, 2014b) in Bologna (who observed three maxima during the day for the wastewater flow rate) and Matos et al. (2013) in Portugal (who studied the timing of bath, washbasin, sink and toilet use).

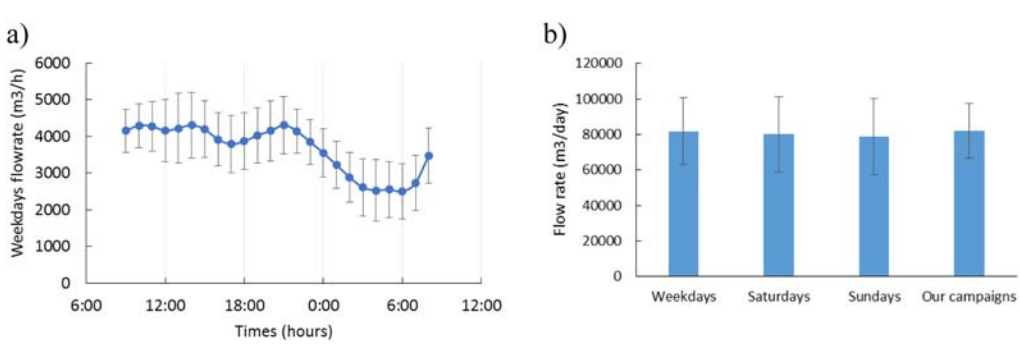

Fig. 2. Average hourly flow rate variations for weekdays (a) and daily average flow rate (2009–2014) (b). The vertical bars represent $\pm$ the standard deviation in both graphs.

The flow rate recorded during our Saturday campaign varied from 1429 to 3449 m^3/h, with an average of 2460 ± 650 m^3/h, for a daily flow rate of 59,043 m^3/day. The daily variation is similar to that during the weekdays. This observation indicates that the habits of daily water consumption do not change substantially between Saturdays and weekdays, with residents and visitors showing similar morning, midday and evening activities. However, there is a delay of 2 h in the appearance of the first peak (approximately at 12:00 am). This delay of the first peak during the day for weekend flows was also observed in Bologna in Italy by Cippola and Maglionico (2014a, 2014b). According to the SIERM data for dry weather conditions, the average flow rate decreases by 2% and 9% on Saturdays and Sundays, respectively (Fig. 2b).

Fig. 3a presents the variation in the average daily ammonium concentrations in the sampling campaigns together with the variation in ammonium recorded on Jan 21, 2016. The main source of ammonia in sewage is urine, as urea, its main component (≈2%) after water (95%), is rapidly transformed into ammonia. Two maxima can be observed: the main one, recorded at the end of the morning, corresponds to the voiding of the bladder after the night. A secondary maximum is observed in the evening. During the day, the ammonium level varies from 16 to 50 mg/L, with an average of 32 ± 9 mg/L. The flow rate is significantly correlated with ammonium ($R^2 = 0.8$). A 7% load decrease is observed between the weekends and weekdays for ammonium and Kjeldahl nitrogen (TKN) according to the SIERM database (Fig. 3b), but the average concentrations are similar (37 mg/L for weekdays and 36 mg/L for weekends for NTK and 26 mg/L for weekdays and 25 mg/L for weekends for ammonium). Based on the design load of 15 g/N/pe (where pe = person equivalent) used in France (2006-03 French decree), a daily load of 2900 kgN corresponds to a population of 193,000 pe, to be compared with the municipal population of 274,000 inhabitants and a potential population of 374,000 inhabitants. A very detailed comparison is difficult, as the age distribution is not taken into account (youngsters, which represent 15% of the total resident population of the catchment (Figure SI3), are likely to excrete less ammonium per individual) and because most of the ammonia associated with incoming workers is excreted at their place of residence (before work and after work) and not at their place of work.

Daily O-phosphate ranges from 3 to 12 mgP/L, with an average of 6 ± 3 mg/L, with variation very similar to that of ammonium (Fig. SI5 of Supporting Information). The average value is itself very similar to the value found by Houhou et al. (2009b) between 2004 and 2006. In Nancy, approximately 20% of the total P is particulate P. There is a statistically significant correlation with ammonium, with a coefficient of determination of $R^2 = 0.9$. Phosphorus in sewage has an anthropogenic origin: it is released through urine and feces in toilets (from 60% (Comber et al., 2013) to 85% (Gray and Becker, 2002)) and detergents. The total phosphorus load decreases during weekends (9% for Saturdays and 14% for Sundays, w.r.t weekdays). The larger decrease with respect to ammonium and TKN could be related to a decrease in cleaning activity, especially in commercial and office buildings during weekends. The legal design basis for P removal of 4 gP/pe/day (2006-503 French decree) corresponds to a population of 96,000 on weekdays and 83,500 on Sundays, which is much lower than the municipal population. In a recent study in the UK (Comber et al., 2013), a value of 2.03 gP/pe/day was calculated for the phosphorus load due to domestic usage. Such a value will double the potential population in the Grand Nancy catchment.

Figures SI6a and SI6d present the average daily variation in total COD and DOC. A large standard deviation is observed for the total COD throughout the day; this might be due to the use of a micromethod to measure the total COD. Our total COD values, ranging from 133 to 318 mg/L, with an average of 226 ± 53 mg/L, are lower than the values provided by the SIERM database (Fig. SI6c). Considering the large standard deviation, it is difficult to determine when the daily maximum occurs. For DOC as well as turbidity (Fig. SI6e), smaller standard deviations were obtained, and three maxima were observed during the day; their timing corresponds approximatively to the timing of the flow rate maxima. Early morning and evening activities, as well as lunch breaks brings a lot of greywater resulting from washing in the sewer system. The total COD and DOC were significantly correlated with turbidity ($R^2 = 0.8$ for COD and 0.9 for DOC). This result can be explained by the turbidity being largely due to particulate matter of organic origin (food debris, disintegrated feces, toilet paper, etc.) and by the simultaneous transport of particulate and dissolved organic pollutants.

A weekend effect is clearly seen in the total COD loads (10% and 20% decrease for Saturdays and Sundays, respectively), total COD concentrations (8% and 16% decrease for Saturdays and Sundays, respectively) and BOD_5 loads (15% and 24% decrease for Saturdays and Sundays, respectively). These decreases are larger than those for ammonium and could reflect a shift in human activities, with less pollution related to work, especially to cleaning and catering (lunches).

The pH values range from 7 to 8, with 1% for the variation coefficient and an average of 7 ± 0.1 (Fig. 4a). The pH, although varying slightly during the day, remains practically constant and does not show clear daily dynamics; this indicates the high buffering capacity of the wastewater. Correspondingly, the electric conductivity (Fig. 4b) has an hourly value ranging between 906 and 1234 μs/cm, with average value equal to 1032 ± 81 μs/cm and a coefficient of variation of 8%. The electrical conductivity (χ) is a linear function of the concentrations (C_i) of the n ions, mobility (λ) and charge (z) present in a liquid sample (Eq. (1)):

$$\chi = \sum_{1}^{n} \lambda_i C_i z_i \tag{1}$$

The daily variation in the main cations and anions (except ammonium (Fig. 3a) and O-phosphate (Fig. SI5)) are presented in Figure SI7. The overall mineralization of the water does not vary much over the day.

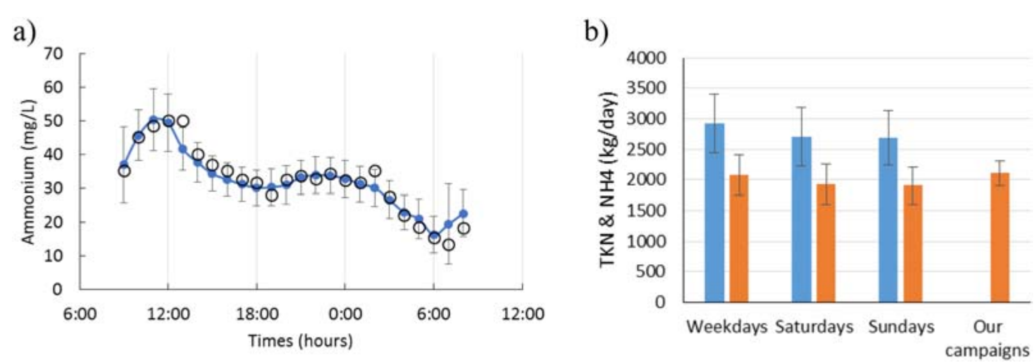

Fig. 3. Average hourly ammonium variations for weekdays (close symbols) and ammonium variation for Jan 21, 2016 (a) and daily ammonium (blue bars) and NTK (orange bars) average loads (2009–2014) (b). The vertical bars represent ± the standard deviation in both graphs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

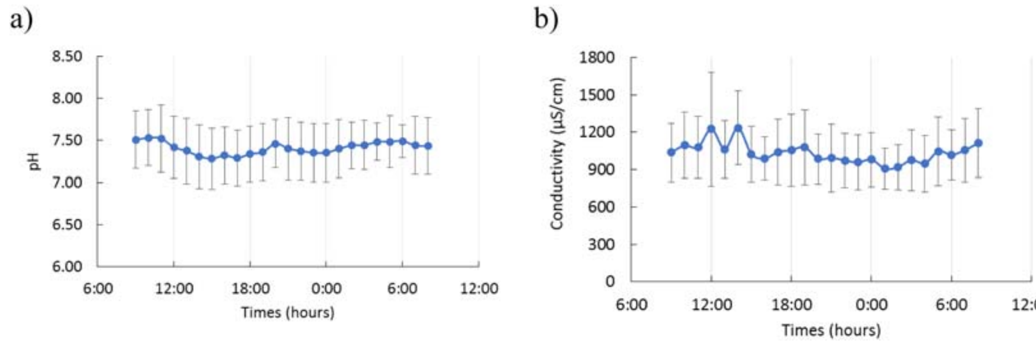

Fig. 4. Average hourly pH (a) and conductivity (b) variations for weekdays. The vertical bars represent ± the standard deviation in both graphs.

The electrical conductivity due to K^+, Na^+, Ca^{2+}, Mg^{2+}, NH^{4+}, Cl^-, SO_4^{2-} and PO_4^{3-} was calculated, and Ca^{2+} is the ion with the greatest contribution (28% ± 3%). Ammonium is the fourth highest contributor (10.6% ± 2.8%) after Cl^- (23.8% ± 2%) and Na^+ (17% ± 2%). Cl^- and Ca^{2+} have maxima at the end of the night, when ammonium reaches a minimum; this pattern can explain the relative stability in conductivity throughout the day. There might be different explanations for the increase in calcium concentration at the end of the night, such as sewer corrosion (de Belie et al., 2004) or dissolution of the different Al-Ca-phosphate minerals that can be found in sewer sediments (Houhou et al., 2009a). Potassium, whose origin is mainly linked to human metabolism, is linearly positively correlated with ammonium ($R^2 = 0.7$).

The orders of magnitude of the variation in total metal concentration are presented in Table SI3, with the order of decreasing contribution based on average concentration being Al > Zn > Mn > Cu > Ni > Pb > Cr > Cd > Co. The prevalence of zinc and copper is in agreement with results in the literature (Houhou et al., 2009a, 2009b), and these metals are highly related to household activities.

Figure SI8 presents the daily variation in copper, zinc and aluminum. Due to the large standard deviations found for these minerals, a detailed analysis of this variation is difficult. However, the copper concentration is minimal during the night, with several maxima occurring during the day. Copper can be released in wastewater from drinking water pipes but also via feces (Zorbas et al., 2004). Zinc can be released via plumbing and feces (Zorbas et al., 2003), similar to copper. It is also present in detergents (Zoller, 2009). Due to its antiseptic properties, it is also widely used in toothpastes, mouthwashes and shampoos, which can partly explain its release in the evening and early morning.

4. Conclusion

The detailed analysis of daily commutes into and out of a large urban catchment reveals that the total population can increase during the working hours, therefore causing more pollution than what can be expected from the simple consideration of the municipal population. Census data are very useful for this purpose and their availability may depend upon the country. Furthermore, variation in the activities of the population in a catchment, in particular the existence of lunch breaks of different durations or different timing for the evening meal which are function of the local way of life, also need to be taken into account to provide realistic models of the wastewater flow rate and pollution parameters. In general it is suggested to pay more attention to social parameters to discuss wastewater dynamics. The anticipation of pollution load variations could be taken into account in the definition of the WWTP control strategy, such as the optimization of aeration and/or external carbon feeding for denitrification.

Although most pollution-related parameters (COD, ammonium, etc.) exhibit diurnal variation, this might not be the case for pH and conductivity. This phenomenon is due to the different dynamics of the anions and cations and might be catchment dependent. These data are rarely considered and could be of high interest in the development of resource recovery processes where they are involved.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.12.087.

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