Arsenic mass balance in a paper mill and impact of the arsenic release from the WWTP effluent on the Moselle River
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ABSTRACT
Rivers used for drinking water production might be subject to anthropogenic pollution discharge upstream of the intake point. This problem was investigated in the case of the Moselle River, used for water production in Nancy (350,000 inhabitants) and which might be impacted by industrial activities 60 km upstream. The arsenic flux of a pulp and paper mill discharging in the Moselle River at this location has been more specifically investigated. The main sources of arsenic in that mill seemed to be the recovered papers and the gravel pit water used as feed water. The arsenic input related to wood and bark was limited. The main arsenic outputs from the plant were the paper produced on site and the deinking sludge. The arsenic concentration in the effluent of the wastewater treatment plant (WWTP) was not correlated to the one in the gravel pit water, but may depend on the operating conditions of the WWTP or the changes in processes of the mill. The impact of this anthropogenic source of arsenic on the Moselle River was slightly larger in summer, when the flowrate was lower. Globally the impact of the paper mill on the Moselle River water quality was limited in terms of arsenic.

Key words | arsenic, deinking, effluent, pulp and paper mill, sludge

INTRODUCTION
Because of its toxicity, presence of arsenic in groundwater and surface water has become of high concern (Cullen & Reimer 1989; Jain & Ali 2000; Smedley & Kinniburgh 2002; Choong et al. 2007). The limit of arsenic concentration for drinking water quality has been set to 10 µg/L in the guidelines for drinking-water quality (WHO 2008). This value has been taken as maximum allowable value for arsenic concentration of drinking water in France in 2001.

The source of the Moselle River is in the North East of France. It flows through France, Luxembourg and Germany, and its water serves as source of drinking water for many cities, as Nancy (350,000 inhabitants) in France. However, many industries (metallurgy, pulp and paper) are discharging their treated effluent into this river. This is the case for a pulp and paper mill located at Epinal, 60 km upstream of Nancy. It is known that this type of industry is a big water user. Although arsenic is a non-process element, the plant managers as well as water quality authorities are concerned by the possible influence of such a large plant on the Moselle River, whose flowrate near the discharge point is very variable.

The presence of trace elements and pollutants in the pulp and paper industry has been studied from different points of view. Skipperud et al. (1998) studied the transfer, pathways, enrichment and discharge of trace elements (except arsenic) in a pulp industry in Norway. Pokhrel & Viraraghavan (2004) reviewed the treatments of pulp and paper wastewater concerning the main pollutants. Bryant & Pagoria (2004) studied the fate of metals in forestry wastewater treatment systems, and gave some information on metal concentrations in the effluent but they did not study the impact of those metal concentrations on the receiving water system. Holmbron et al. (1993) looked at the effect of a pulp and paper mill on metal concentrations in a lake.

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system. They found that most metal concentrations were relatively low in the effluent. However, due to the large effluent flow, the discharged quantities were considerable for some nontoxic metals. A study about dangerous substances for the aquatic environment present in industrial and urban wastewater in France (INERIS 2008) highlights the presence of arsenic in pulp and paper mill effluents, but downplays the fact because of the presence of arsenic in the feed water.

The purpose of this work was to study the arsenic sources and discharges of a pulp and paper mill, and to evaluate the impact of the arsenic discharge from its wastewater treatment plant (WWTP) effluent on the Moselle River. The arsenic mass balance on the paper mill has been established by studying the arsenic concentration and the flow rates of all inputs and outputs. The impact of the arsenic release was evaluated by comparing the arsenic amount discharged to the increase of the arsenic concentration in the Moselle River at the discharging point.

**RESULTS AND DISCUSSION**

**Description of the pulp and paper mill**

Figure 1 shows the flowsheet of the pulp and paper mill. The WWTP is composed by a primary settling treatment, a secondary biological treatment by activated sludge, and a tertiary chemical treatment based on flotation, and, depending on the effluent quality and the Moselle River’s flowrate, coagulation/floculation by addition of aluminum sulfate and anionic polymer. The WWTP effluent is then discharged into the Moselle River. The paper is produced on site from thermomechanical wood pulp as well as deinked pulp (flotation deinking). The water treatment process pumps water from a gravel pit, and leaching procedure (US EPA method 1312 1994) at pH = 4.2, and the WWTP effluent at pH = 7.4. The influence of the particle size of bark was also analyzed using four ranges of particles size with the WWTP effluent as the leaching solution: 0.112–0.200 mm, 0.200–1 mm, 1–2 mm, and >2 mm.

**Preparation of samples and analysis**

Solid samples were dried at 105 °C in a drying oven. Bark and wood samples were then ground. Paper samples were cut in pieces of 5 mm. The solid samples (about 1 g) were mineralized by digestion with nitric acid and hydrogen peroxide at about 90 °C. Nitric acid (70%, laboratory reagent grade, Fisher Scientific) and hydrogen peroxide (50%, Prolabo) were added until no more oxidation occurred. The acid digestion of aqueous samples (50 mL) was carried out with 10 mL of nitric acid (≥65%, puriss. p.a. grade, Sigma-Aldrich) and 3 mL of 30% aqueous hydrogen peroxide (Prolabo) at about 90 °C.

The digested sample was then diluted to 50 mL with deionised water and filtered at 0.45 µm. Finally superpure HNO₃ (for trace analysis, Carlo Erba) and indium (in solution) were added in order to obtain 10 µg/L of indium as internal standard and at least 5% HNO₃.

Total arsenic concentration was measured with an inductively coupled plasma mass spectrometry (ICPMS, Series X7 Thermo) instrument equipped with a collision/reaction cell (C/RC) and a CETAC autosampler. A gas mixture of helium (93%) and hydrogen (7%) was used for the C/RC.
consists in disinfection/oxidation by ClO₂ followed by filtration on sand beds to retain the precipitated compounds (mainly iron and manganese oxides). Two drying processes are used, one for the deinking sludge and the other one for the WWTP sludge. The dry sludges are then incinerated on site with other solid fuels as bark, urban sludge, energy wood and plastics. The filtration of the WWTP effluent produces the process water 2 which is mainly used in the deinking process, but also for the watering of the logs in the storage area during summer to maintain their humidity. The arsenic input due to the chemical products used in the plant was not taken into account in this study. On one hand, arsenic may only be present as trace element in the chemical products. On the other hand, the flow rate of all the chemical products entering the plant is negligible compared to the other ones. Thus, the chemical products are not a major source of arsenic in the plant. The mass balance of arsenic was done on the whole plant (Table 1). The pulp and paper mill was viewed as a black box where all the processes are lumped together.

### Arsenic contents of inputs

The sources of arsenic entering the plant are recovered papers, wood and bark leachates from the storage area,的心情与期待。考虑到 Arthur’s Cottage的地理位置和它所代表的文化特征，会让人联想到一个宁静的乡间小屋，一个与城市喧嚣隔绝的地方，享受着自然的馈赠和历史的沉淀。 Arthur’s Cottage的独特魅力和它所承载的英国文化，无疑会吸引那些热爱探索历史和自然美的旅行者，让他们在这里找到内心的平静和灵感的源泉。无论是欣赏湖光山色，还是品味当地的美食，Arthur’s Cottage都能提供一个理想的环境，让人心旷神怡，流连忘返。
The arsenic concentration of the gravel pit water has been measured monthly since 2000 (Figure 2 (a)). For the other sources of arsenic, the arsenic concentration was measured in samples from 2008 and 2009, but the average flux was calculated according to the average flow rate of the last 10 years (Figure 3).

Based on the arsenic concentration measured in the recovered papers taken in the stocks in 2008 and 2009,
the main source of arsenic seemed to be the recovered papers. However, the arsenic concentration in recovered papers may vary with time. In a preliminary study made in 2005 0.9 mgAs/kg d.w. (dry weight) was measured in the recovered papers. Moreover, Manso et al. (2007, 2008) show very different arsenic concentrations in paper, from below the detection limit to 2000 mgAs/kg, depending on the date and on the location of production. Therefore, even if the arsenic concentration in recovered papers may vary with time, its flow rate is so large that the recovered papers are likely to remain the main source of arsenic for the pulp and paper mill.

Nevertheless, the arsenic flux of the gravel pit water was not negligible. The water used in the processes of the plant (process water 1) comes from a gravel pit and is treated prior to use. There are seasonal variations of arsenic concentration in the water of the gravel pit around the year (Figure 2(a)) with an increase during summer. This increase may be due to larger leaching of arsenic from the gravel pit substratum under elevated temperature.

The arsenic concentration was higher in bark than in wood (Table 1). This may be due to the absorption of arsenic particles from the air in addition to the absorption of arsenic compounds from the soil (Saarela et al. 2005; Cheng et al. 2007). Leaching of arsenic from bark (from the stock of bark or when logs in the storage area are watered or due to rainfalls) could transfer arsenic to the WWTP. The pH of the leaching solution as well as the particles size of the bark did not exhibit a drastic influence on arsenic leaching (data not shown). From those experiments, the maximum arsenic concentration of bark leachates, equal to 6 µg/L, was chosen for the estimation of its arsenic flux. But globally, the arsenic inputs related to wood and bark were limited.

**Arsenic content of outputs**

Outputs from the plant are the WWTP effluent, the dry sludge produced by the deinking process and by the WWTP process, and the paper produced by the paper mill. The main arsenic outputs seemed to be the paper produced on site as well as the deinking dry sludge. This is likely to be due to the arsenic content of the recovered papers from which the paper and the deinking sludge are produced.

The average arsenic fluxes of the gravel pit water and of the WWTP effluent were very similar. However, these fluxes were not correlated since there was no seasonal variation of the arsenic concentration observed in the WWTP effluent (Figure 2(b)). Moreover, the arsenic flux of the gravel pit water tended to be larger than the flux of the WWTP effluent. The presence of arsenic in the WWTP influent, and therefore in the WWTP effluent, is due to the combination of all the effluents of the processes in the pulp and paper mill (Figure 1). The effluent from the water treatment process is only one among the others. Furthermore, the water treatment of the gravel pit water is efficient in removing arsenic since it is based on the oxidation of manganese and iron compounds followed by filtration on sand beds (Kartinen & Martin 1995; Gregor 2001). This process produces an arsenic-rich sludge which is likely to be removed by the primary settling stage of the WWTP, thus this arsenic content should finally be in the WWTP dry sludge. The variation of the arsenic concentration in the WWTP effluent is partly due to the coagulation/flocculation process of the tertiary treatment of the WWTP, which is known to be an arsenic removal technology (Kartinen & Martin 1995; Gregor 2001). However, there were also decreases of the arsenic concentration in the WWTP effluent without tertiary treatment being in operation (no addition of aluminum sulfate). The increase of the arsenic concentration between 2005 and 2006 is still not explained effectively. The main assumption is that it results from the combination of several documented or un-documented disturbances during this period, some of them being changes made in the deinking process.

**Characteristics of the Moselle River**

The plant is located upstream to Nancy, in the industrial area of Epinal (60,000 inhabitants), Nancy (350,000 inhabitants) and Metz (250,000 inhabitants) are two large cities downstream (Figure 4(a)). The Moselle River water is used as a source of drinking water for Nancy. The arsenic concentration has increased along the Moselle River between February and July 2007 (Figure 4(b)), which was most likely due to anthropogenic sources of arsenic. After that period, the concentrations were very similar at the different locations along the river, and were mostly lower than
3 µgAs/L. At location 1, which is downstream from the discharging point of the plant, the arsenic concentration was stable and lower than 4 µgAs/L in 2007 and 2008. On the contrary, the arsenic concentration at locations 5 and 6 varied significantly, and was above the allowed arsenic concentration of 10 µgAs/L for drinking water (WHO 2008) during the first months of 2007. The Moselle flow rate is very variable with low water during summer months (Figure 4(c)). Between 2000 and 2009, the monthly average flow rate at Epinal was equal to 37 m³/s with a minimum flow rate of 3 m³/s, and a maximum flow rate of 126 m³/s.

Figure 4 | (a) Geographical context of the Moselle River; (b) arsenic concentration in the Moselle River (source: AERM) and (c) yearly variation of the Moselle River’s flow rate at Epinal (source: DIREN Lorraine).

Figure 5 | (a) Arsenic flux in the WWTP effluent and (b) increase of the arsenic concentration in the Moselle River due to the arsenic amount of the WWTP effluent.
Impact of the WWTP effluent on the Moselle River

The impact of the effluent on the Moselle River was evaluated by comparing the arsenic amount discharged in the Moselle River (Figure 5(a)) to the increase of the arsenic concentration in the Moselle River at the discharging point (Figure 5(b)). There was no seasonal variation of the arsenic flux in the WWTP effluent. Actually, the maximum amount of arsenic in the WWTP effluent occurred in November 2003 and April 2004. Moreover, the arsenic flux of the WWTP tends to be lower between July and October. Despite this, the arsenic concentration added to the Moselle River was small with an average increase lower than 0.15 µgAs/L. Globally, the arsenic concentration added to the Moselle River was larger during those months due to the flow rate of the river being much lower. It was actually the case in August 2003 (2003 was a severe drought year in Western Europe) when the arsenic concentration in the Moselle River increased by 0.8 µgAs/L at the discharge point while its flow rate was the lowest on the period 2000–2009. Except in 2003, the arsenic concentration added to the Moselle River was small with an average increase lower than 0.15 µgAs/L. Globally, the impact of the paper mill on the Moselle River water quality is limited in terms of arsenic.

CONCLUSION

This study focused on the characterization of the arsenic fate in a pulp and paper mill, as source of anthropogenic arsenic in a drinking water resource. The main sources of arsenic in the plant seemed to be the recovered papers and the gravel pit water. The variation of the arsenic concentration in recovered papers is not well known. Therefore, only an estimation of this arsenic flux was possible. The main arsenic outputs were the paper produced on site and the deinking dry sludge produced by the deinking process of the recovered papers. Furthermore, the arsenic concentration of the WWTP effluent may vary significantly. Part of this variation is due to the tertiary treatment of the WWTP using coagulation/flocculation process. The flow rate of the Moselle River next to the discharging point is very variable throughout the year, and may be very low during summer. This causes an increased risk of adding larger arsenic concentration to the Moselle River, despite the arsenic flux from the WWTP effluent being reduced. Nevertheless, the average increase of the arsenic concentration in the Moselle River at the discharge point stayed below 0.15 µgAs/L throughout the year.

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REFERENCES


