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Polycyclic Aromatic Hydrocarbons and *n*-alkanes in sediments of the Upper Scheldt River  
Basin: contamination levels and source apportionment

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### Summary

The Scheldt River system is located in northern France, Belgium and the Netherlands and includes a dense network of rivers, which contributed to the urban and industrial development in this area. Three sediment cores, collected in the Upper Scheldt River (Helkijn) and two of its tributaries (the Lys River at Wervik and the Espierre Canal), were analysed for *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs). Total *n*-alkane and PAH concentrations in all the sampled cores ranged from 2.8 to 29 mg kg<sup>-1</sup> and from 4.9 to 96 mg kg<sup>-1</sup>, respectively. The contributions of biogenic, petrogenic and pyrolytic sources were investigated using *n*-alkane indexes and PAH diagnostic ratios. *n*-alkane chromatograms were characterized by the predominance of odd over even long chain *n*-alkanes (produced by terrestrial plants) and by the occurrence of a broad unresolved complex mixture (UCM) which evidenced biodegraded petroleum residues. For the three studied cores, correlations between the concentrations of UCM and *n*-alkanes (both expressed on an organic carbon basis) indicate a common origin or similar pathways of these allochthonous compounds to the aquatic environment. Wervik sediments were distinguished by higher *n*-alkane concentrations and by a major aquatic biogenic source for low molecular weight *n*-alkanes. The prevalence of combustion-derived PAHs was indicated by the high contribution of four, five and six rings compounds and was confirmed by isomer ratios. Higher levels of low molecular weight PAHs in Helkijn surface sediments suggested modest petrogenic inputs in this navigable canal. High PAH concentrations in Espierre sediments could be explained by a major historical contamination from urban and industrial emissions.

## 1 Introduction

The study area for this research was the Upper Scheldt and two of its tributaries: the Lys River and the Espierre Canal. The Scheldt River flows through France, Belgium and the Netherlands in one of the most industrialized and urbanized areas in Europe. Ten million people live in the Scheldt River Basin and the population density can reach 2000 inhabitants km<sup>-2</sup> close to cities like Lille and Antwerp. Anthropogenic activities including textile and chemical industries, transport, coal mining, paper mills and metallurgical plants have contributed to the extensive contamination of aquatic ecosystems since the middle of the 19th century. The water quality in the Scheldt River Basin is now of a great concern for France, Belgium and the Netherlands. Since 2002, the International Scheldt Commission (ISC) has been developing an integrated and coordinated water management plan for the whole river basin in this way preparing the implementation of the Water Framework Directive of the European Parliament and of the Council of the European Union (WFD).<sup>1</sup>

Most previous studies of contamination in the Scheldt River focused on the estuary<sup>2-4</sup> or on soils affected by dredged sediments<sup>5</sup>; much less information is available on water quality in the upper river. This gap in knowledge was partly filled by the INTERREG III - STARDUST European Research Program for trace metals in river sediments<sup>6,7</sup>, but data on hydrocarbon contamination are still scarce. Two classes of hydrocarbons where data are lacking are polycyclic aromatic hydrocarbons (PAHs) and *n*-alkanes.

The proven mutagenic and carcinogenic effects of some PAHs as well as their bioaccumulation and persistence in the environment<sup>8</sup> have lead the United -States Environmental Protection Agency (US EPA) and the European Union to include PAHs in their lists of priority pollutants. PAHs derive from the incomplete combustion of organic matter including biomass and fossil fuels (pyrolytic source), from the spillage of petroleum or refinery products (petrogenic source)<sup>9</sup>, and from the post-depositional degradation of biogenic precursors (diagenetic source).<sup>10</sup> PAHs enter the aquatic environment through runoff from contaminated roads or sealed parking lots<sup>11</sup>, urban and industrial waste water discharge, direct spillage and wet and dry deposition of atmospheric born contaminants.<sup>12</sup> *n*-alkanes can be of petrogenic origin or produced by a variety of terrestrial and aquatic organisms.<sup>13,14</sup> Owing to their hydrophobic character and affinity toward particulate matter, hydrocarbons tend to accumulate in sediments.<sup>15</sup> These contaminated sediments represent a potential threat and source of exposure to aquatic organisms by release to the overlying water column.<sup>16</sup>

Objectives of this study are to assess the contamination levels and to determine the hydrocarbon fingerprint and sources of pollution in the Upper Scheldt River Basin. Different

qualitative and quantitative indexes based on *n*-alkanes and PAHs are used for source apportionment of hydrocarbons in sediments. Data are also discussed in terms of trends with depth in sediment cores.

## **2. Materials and methods**

### **2.1 Study area and sampling**

The Scheldt River has a catchment area of 21860 km<sup>2</sup>. It flows over the northern European plain and thus has a very low gradient, about 100 m fall between its source and the estuary. Sediment cores were collected from three sites in November and December 2005 (Fig. 1). Sampling site Espierre (Fig.1, site 1) is on the Espierre Canal approximately 100 m upstream from the confluence with the Scheldt River. The Espierre Canal was built in the middle of the 19<sup>th</sup> century to connect the Deûle River (in France) to the Scheldt River (in Belgium) and thus to supply water and coal to the city of Lille, which at that time was experiencing rapid industrial growth. The water quality in the Espierre Canal declined quickly owing to the discharge of urban and industrial waste waters and the canal was closed for navigation in 1985. Sampling site Helkijn (Fig.1, site 2) is on the Scheldt River approximately 200 m upstream from the lock at Helkijn and downstream from the confluence with the Espierre Canal. Barges of up to 1500 tons can navigate in this part of the Scheldt River. Sampling site Wervik (Fig.1, site 3) is on the Lys River in a meander which is used for yachting, near the junction with the canalised part used for the navigation of barges. With the implementation of the European water framework directive (WFD) <sup>1</sup>, the Espierre Canal and the Lys and Scheldt Rivers are considered as heavily modified water bodies.

For each site, two sediment cores of approximately 25 cm length and 10 cm diameter were sampled by a diver: one for pH and redox potential measurements (see section 2.2) and one for further analysis (see sections 2.3 and 2.4). This last core was sectioned in 2 cm slices and each slice was homogenised before being transferred into pre-combusted aluminium containers capped with aluminium foils. Sediment samples were stored in a freezer (-20°C) until extraction and analysis.

### **2.2 Redox potential and pH measurements**

In the field, redox potential and pH were measured in sediments by inserting specifically designed electrodes through pre-drilled holes. These holes (1 cm intervals) were covered with adhesive tape during sample collection. Redox potential and pH measurements were done using respectively a combination glass electrode (Ingold) and a combination platinum

electrode (Mettler Toledo/Pt 4800). The reference electrode Ag/AgCl, was used for both pH and redox potential measurements.<sup>6,7</sup>

### 2.3 Organic carbon analysis and granulometry

The sediment organic carbon (OC) was measured using a CHNS-932 (LECO) elemental analyser. Sediment samples were dried at room temperature to constant weight, ground and sieved (1 mm). Total carbon was measured just after sieving. Then, sediment samples were heated at 450°C during 12 hours in order to remove organic carbon.<sup>17</sup> OC content was calculated as the difference between the two measurements. Samples were analysed in triplicate and calibration was carried out using known amounts of cysteine (C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>NS). The detection limit was 0.01 mg of carbon per gram of dried sediment. Organic carbon content is later expressed as a relative mass fraction in %.

Grain size distribution was determined on wet sediments by laser granulometry (Malvern Mastersizer 2000) in the analytical range 0.02-2000 µm.

Sedimentation rates or isotopic dating have not been determined in these sampling locations since navigation and/or dredging can alter the chronological deposition of sediments.

### 2.4 Analytical procedure

Sediment samples were dried at room temperature, ground and sieved at 1mm. Analysis were performed on the <1 mm fraction. Sediments were analysed for *n*-alkanes (from *n*-C12 to *n*-C34) and for the following non-alkylated polycyclic aromatic hydrocarbons (PAHs): naphthalene (N), acenaphthylene (Acy), acenaphthene (Ace), fluorene (F), phenanthrene (P), anthracene (A), fluoranthene (Fl), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene + triphenylene (Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IdP), dibenz[*ah*]anthracene (DA), benzo[*ghi*]perylene (BPer). The 16 analysed PAHs include those listed on the European Union priority pollutants lists.<sup>1</sup>

Samples were spiked with deuterated internal standards (N-d8, P-d10, Pyr-d10, Per-d12 purchased from LGC-Promochem) for the quantitation of PAHs and with eicosene (purchased from Dr Ehrenstorfer GmbH) for the quantitation of *n*-alkanes. After a delay of equilibration, sediment samples were extracted using an accelerated solvent extractor (ASE 200, Dionex) under the following conditions: extraction solvent hexane/acetone (1:1,v/v), 2 static cycles of 5 minutes, 150°C, 14 Mpa, 60% of flush. Molecular sulphur was precipitated by adding activated metallic copper to the extracts. Extracts were purified and fractionated by liquid chromatography on a silica column. Aliphatic and aromatic hydrocarbons were respectively

recovered with the elution of hexane and of a mixture of hexane and dichloromethane ((3:1,v:v) and (1:1,v:v)). Each fraction was concentrated using a rotary evaporator and a slight stream of nitrogen before gas chromatography (GC) analysis.

PAHs were analysed using a Varian 3900 gas chromatograph equipped with a deactivated fused-silica guard column (5m, 0.53 mm i.d.) and a fused-silica capillary column coated with VF-5ms (30 m length, 0.25 mm i.d., 0.25  $\mu$ m film thickness, Varian Inc.) and coupled with an Ion Trap Saturn 2000 Mass Spectrometer. The carrier gas was helium at a constant flow rate of 1 mL min<sup>-1</sup>. Samples were injected in the splitless mode at 280°C and the injector was purged with helium after 1 min. The temperature of the GC oven was programmed as follows: from 70°C (2 min) to 150°C at 25°C min<sup>-1</sup>, then to 280°C at 5°C min<sup>-1</sup> (held for 10 min). The transfer line and the ion trap were respectively held at 280°C and 240°C. PAH identification was done on the basis of the retention time and the mass spectrum and quantitation was performed in the single ion storage (SIS) mode, using the most abundant ion. Response factors were determined relative to the deuterated PAH response and to a mixture containing the 16 PAHs (Calibration mix SV 5, Restek) and the four deuterated standards. Four deuterated standards were used in order to better fit to the properties of each group of PAHs.

*n*-alkane analysis was performed on a Varian 3800 gas chromatograph equipped with a deactivated fused-silica guard column (5m, 0.53 mm i.d.) and a Rtx-5Sil MS fused-silica capillary column (60 m length, 0.25 mm inner diameter, 0.25  $\mu$ m film thickness, Restek) and coupled with a flame ionisation detector. The carrier gas was helium at a constant flow rate of 1 mL min<sup>-1</sup>. Injection was performed at 290°C in the splitless mode. The GC temperature program was: from 50°C (1 min) to 100°C (1 min) at 30°C min<sup>-1</sup> and then to 320°C at 10°C min<sup>-1</sup> (held 20 min). The detector temperature was 330°C. Identification and quantification of *n*-alkanes was carried out by injecting a calibration mixture containing *n*-alkanes from *n*-C12 to *n*-C34, pristane and phytane (DRH hydrocarbon mixture, AccuStandard). Unresolved complex mixture (UCM) was quantified using the average response factor of *n*-alkanes.

All chemicals and solvents used were trace analysis or HPLC grade and procedural blanks showed no significant amounts of analytes. Limits of detection were defined as three times the standard deviation of the blank sample and expressed in ng g<sup>-1</sup> of dried sediment. Limits of detection were evaluated to 5.0 ng g<sup>-1</sup> for *n*-alkanes and to 0.5 ng g<sup>-1</sup> and 1.5 ng g<sup>-1</sup> for low molecular weight PAHs and high molecular weight PAHs respectively. The total procedure uncertainty, determined on a triplicate extraction of one of the river sediments, was 7.0 – 8.3 % for *n*-alkanes and 2.2 – 2.8 % for PAHs (depending on the compound). The certified reference sediment NIST SRM 1944 (purchased from LGC-Promochem) was used to check

on the accuracy of the method. Average recoveries varied from 60.2 % (acenaphthene) to 127.2 % (chrysene). Recoveries greater than 75 % were generally achieved with the exception of acenaphthene (60.2 %) and fluorene (66.1 %).

Statistical analyses were performed using the software StatBox version 6.6.

### **3. Results and discussion**

#### **3.1 Sediment properties**

The strongly anoxic character of the sediments was confirmed by redox profiles and by absence of dissolved oxygen from the first mm of sediment. Oxygen concentrations in pore waters were measured by an O<sub>2</sub> microsensor fixed to a micro-manipulator and connected to a pico-ammeter (Unisense).<sup>7</sup> Redox potential and pH measurements have been done jointly with Lesven *et al.* (2008)<sup>7</sup> in the framework of the french-belgian INTERREG III - STARDUST program (see this reference for the resulting pH and redox potential profiles). The redox potential shows slightly negative values just below the sediment–water interface with a rapid decrease to a mean value of –200 mV (Ag/AgCl) for Wervik and Helkijn sediment cores and a mean value of –400 mV (Ag/AgCl) for Espierre core. Redox potential is important to the study of hydrocarbons because biodegradation of PAHs and *n*-alkanes can occur under nitrate- and sulfate-reducing conditions, although degradation rates are lower than under aerobic conditions.<sup>18</sup>

Organic carbon (OC) contents and grain size distributions are summarized in Table 1. OC ranges from 1.5 to 3.7 % for Wervik sediments (maximum at 17 cm depth), from 2.4 to 4.7 % for Espierre sediments (maximum at 17 cm depth) and from 1.7 to 3.1 % for Helkijn sediments (maximum at 5 cm depth). This range of organic carbon is commonly observed in freshwater sediments.<sup>19</sup> Sediments were mainly composed of silt- (4-63 µm) and sand- (63-2000 µm) sized particles (Table 1). The mean d50 were 48.4, 31.2 and 25.6 µm for Espierre, Helkijn and Wervik sediments, respectively. Wervik and Helkijn sediments were similar in terms of grain size with a prominent silt fraction whereas Espierre sediments were more sandy. The sorption of organic contaminants to sediment particles takes place through two types of process: adsorption to mineral and organic surfaces and absorption into organic matter coatings.<sup>20</sup> Smaller particles exhibit a higher surface to volume ratio and have generally a higher organic carbon content.<sup>15,21</sup> As a result, the mass related amount of sorbed contaminants is generally larger in the small-size particle fraction than in the large-size particle fraction. However, for the studied sediments and contaminants, positive and

significant correlation was only noticed for Wervik sediments between the total amount of PAHs and the fine fraction ( $<63\mu\text{m}$ ) ( $r = 0.87$ ,  $p < 0.001$ ).

## 3.2 *n*-alkanes

### 3.2.1 Concentrations and variations in sediment profiles

Chromatograms of the aliphatic fraction presented a suite of resolved *n*-alkanes, ranging in carbon chain length from *n*-C12 to *n*-C34, and two isoprenoids (pristane: 2,6,10,14-tetramethyl pentadecane and phytane: 2,6,10,14-tetramethyl hexadecane), overlying the broad hump of the UCM. Sediment profiles of the total concentrations of resolved *n*-alkanes plus pristane and phytane ( $\Sigma n\text{-alk}$ ) are presented in Fig. 2, expressed on a dry weight basis.

The highest concentrations are recorded for Wervik sediments with a maximum value of  $29.4 \text{ mg kg}^{-1}$  in the first cm and a mean value of  $16.0 \text{ mg kg}^{-1}$  in the rest of the sediment core.  $\Sigma n\text{-alk}$  concentrations range between 2.8 and  $5.5 \text{ mg kg}^{-1}$  for Espierre sediments and maximum values are observed between the surface and 9 cm depth.  $\Sigma n\text{-alk}$  concentrations vary between  $6.0 \text{ mg kg}^{-1}$  (19 cm depth) and  $13.7 \text{ mg kg}^{-1}$  (3 cm depth) for Helkijn sediments. Total concentrations tend to decrease with depth for the three cores. Possible explanations for this decreasing trend can be the biodegradation process occurring with the burial of organic matter or differences in contamination inputs.

### 3.2.2 Source apportionment

Several indexes related to individual compounds concentrations or UCM have been used to distinguish between biogenic (aquatic or terrestrial) and anthropogenic (petrochemical) sources of the aliphatic contamination in sediments. The carbon preference index (CPI) is defined as the ratio of odd to even carbon numbered *n*-alkanes and several ways of calculating this index are presented in the literature.<sup>14,19,22,23</sup> Most abundant *n*-alkanes in biogenic materials, such as epicuticular waxes or algae, generally show an odd predominance and thus CPI values higher than 1. *n*-alkanes *n*-C23, *n*-C25, *n*-C27, *n*-C29 and *n*-C31 are major components of waxes in vascular land plants and the most abundant *n*-alkanes are generally *n*-C15, *n*-C17, *n*-C19 or *n*-C21 for microbial or algae sources.<sup>22</sup> On the other hand, petrochemical derived *n*-alkanes exhibit a wide distribution range, no predominance of odd over even *n*-alkanes and thus CPI values close to 1.<sup>13</sup>

CPI was first calculated on the whole carbon range using Equation 1<sup>24</sup>, fitted to our analytical range.

$$\text{CPI} = [\Sigma (n\text{-C13-}n\text{-C33})] / [\Sigma (n\text{-C14-}n\text{-C34})] \quad (1)$$



CPI values are higher than 1 for all sediments with mean values of 2.6, 2.1 and 2.5 respectively for Espierre, Helkijn and Wervik cores (Fig. 2), suggesting a predominance of biogenic *n*-alkanes in the resolved fraction. To improve the sensitivity of the CPI index, Aboul-Kassim & Simoneit<sup>24</sup> separate the carbon number range into a low (*n*-C12-*n*-C19) range (Equation 2) and a high (*n*-C20-*n*-C37) range (Equation 3) which represent respectively: *n*-alkanes coming from microbiota or volatile fossil fuels and *n*-alkanes originating from terrestrial plant waxes or fossil fuels detritus of urban areas.

$$\text{LCPI} = [\Sigma (n\text{-C13-}n\text{-C19})] / [\Sigma (n\text{-C12-}n\text{-C18})] \quad (2)$$

$$\text{HCPI} = [\Sigma (n\text{-C21-}n\text{-C33})] / [\Sigma (n\text{-C20-}n\text{-C32})] \quad (3)$$

LCPI values are close to 1 all along Espierre (mean value 1.1) and Helkijn cores (mean value 0.8), suggesting a petroleum pollution of these sediments (Fig. 2). On the other hand, Wervik sediments exhibit LCPI values higher than 1 in the first 20 cm (mean value of 3.1) and close to 1 in the bottom of the core (Fig. 2). The contribution of aquatic biogenic *n*-alkanes appears to be predominant for low molecular weight *n*-alkanes in Wervik sediments. Considering the high molecular weight range, HCPI values are higher than 1 for all sediments and show similar vertical profiles as CPI values (Fig. 2), evidencing inputs of biogenic terrestrial materials. The most abundant *n*-alkanes in the studied sediments are *n*-C29, *n*-C27 and *n*-C31 which originate from higher plant waxes. The sum of these three hydrocarbons accounts for 31-53 %, 36-48 %, 45-54 % of the total *n*-alkane contamination respectively for Espierre, Helkijn and Wervik sediments, explaining the positive and significant correlation between CPI and HCPI values ( $r = 0.97, 0.98$  and  $0.79$ , respectively for Espierre, Helkijn and Wervik sediments,  $p < 0.001$ ). These conclusions confirm the usefulness of splitting the carbon range into a low and a high ranges. Because of the predominance of odd and heavy *n*-alkanes, the petrogenic fingerprint appears for Espierre and Helkijn sediments when applying the LCPI index but not when considering the whole range CPI.

Another diagnostic indicator is the UCM (unresolved complex mixture) which is composed of a mixture of branched and cyclic hydrocarbons unresolved by the capillary column and thus forming a hump below the resolved compounds.<sup>25</sup> Chromatograms of unpolluted sediments or samples of biogenic origins are characterised by the absence of hump whereas samples of petrogenic origins (crude oils and some refined fractions such as lubricating oils) show a very large UCM.<sup>26</sup> Wang *et al.*<sup>26</sup> also noticed the occurrence of a UCM in weathered and biodegraded oils and in petroleum polluted sediments. Consequently, the size and the shape of the UCM are useful indicators of the anthropogenic contamination of sediments.<sup>22</sup> All sediments studied show a broad and unimodal UCM eluting between *n*-C16 and *n*-C34. The

maximum of this hump occurred at *n*-C27 for Helkijn and Wervik cores and at *n*-C24 for Espierre core. The ratio of unresolved to resolved compounds (UCM/R) has been used to evaluate the extent of the anthropogenic contribution<sup>14</sup> and indicates contamination by petroleum products when values are greater than 2.<sup>24</sup> The mean UCM/R ratio is 26.0, 8.3 and 9.8 respectively for Espierre, Helkijn and Wervik sediments and no significant variations are observed with depth (Fig. 2). There are positive and significant correlations ( $r = 0.872, 0.944, 0.897$  respectively for Espierre, Helkijn and Wervik sediments,  $p < 0.001$ ) for the three cores between total concentrations of *n*-alkane and UCM concentrations, both expressed in  $\text{mg g}^{-1}$  OC. Such a correlation has been attributed to a common origin of these aliphatic hydrocarbons<sup>13</sup> and/or similar transport pathways and accumulation mechanisms of introduction of these allochthonous compounds to the aquatic ecosystem.<sup>9,27</sup>

The presence of pristane (Pr) and phytane (Ph) is noticed in all sediments. Pristane and phytane are geologic alteration products of the phytyl side chain of chlorophyll in phototrophic organisms.<sup>28</sup> These isoprenoid hydrocarbons commonly occurred in petroleum<sup>27</sup> and have been applied to assess the microbial degradation of petroleum residues in soils and sediments.<sup>23,29</sup> The more complex molecular structure of isoprenoids compared with linear alkanes results in higher resistance to degradation.<sup>28,30</sup> The ratios *n*-C17/Pr and *n*-C18/Ph indicate relatively fresh oil inputs when values are greater than 1 whereas values less than 1 suggest the presence of degraded oil.<sup>14</sup> Serrano *et al.*<sup>30</sup> monitored the natural attenuation of aliphatic hydrocarbons after a simulated diesel spill on an agricultural soil and found a decrease of the ratios *n*-C17/Pr and *n*-C18/Ph during microbial degradation. The *n*-C18/Ph index is  $<1$  for all sediments presented here (Fig. 2) thus confirming the presence of degraded oil residues already indicated by UCM. A decrease in this index is observed for Wervik and Helkijn sites between the first cm of sediment (respectively 0.39 and 0.28) and the bottom of the core (respectively 0.11 and 0.12) pointing out continuous degradation with the burial of organic matter. Espierre sediments exhibit lower *n*-C18/Ph values (mean 0.12) and a decreasing trend in the first 5 cm (0.13 to 0.02) followed by point increase at 9 and 13 cm depth.

### 3.3 PAHs

#### 3.3.1 Concentrations and variations in sediment profiles

Total PAH concentrations, ( $\Sigma$ PAHs, the sums of the 16 parent PAHs analysed expressed on a dry weight basis), are plotted versus depth in Fig. 3 for the three sampling sites.  $\Sigma$ PAHs in Wervik and Helkijn sediments are in the same range whereas  $\Sigma$ PAHs in Espierre are larger

(Fig. 3). In Wervik core,  $\Sigma$ PAHs increases towards the surface in the top 9 cm (from 6.4 to 9.8 mg kg<sup>-1</sup>) and exhibits two subsurface maxima (at -15 and -23 cm).  $\Sigma$ PAHs in Helkijn core increases in the top 5 cm and show three subsurface maxima (at -11, -15 and -21 cm). The level of the PAH contamination is much higher in Espierre sediments, but the general trend is downward, with concentrations decreasing from a maximum of 96 mg kg<sup>-1</sup> at a depth of 15 cm to about 40 mg kg<sup>-1</sup> in surface sediment. The concentration at the bottom of the core is 60 mg kg<sup>-1</sup>.

The higher concentrations in Espierre sediments probably reflect the strong historical inputs due to urban and industrial emissions in the watershed. The Espierre catchment has a great number of current and former industrial and polluted sites and extensive urbanization including parts of Lille and its suburbs. The decrease in  $\Sigma$ PAHs in recent Espierre sediments could indicate improvements in water quality since waste water treatment developed and since industrial activity decreased in this area.

The European water framework directive establishes threshold values for PAH concentrations in water but, at present, concentrations in sediments are not taken into account when assessing the ecological quality status of a water body. Sediment potential toxicity was thus evaluated by comparison with a sediment quality guideline (SQG) used in the United-States. SQGs for PAHs rely on theoretical, laboratory, and field foundations and on large databases allowing for the investigation of correlations between chemistry (contaminant concentrations) and biology (effects measured on the aquatic fauna).<sup>31</sup> Numerous approaches have been proposed to assess the potential toxicity of a PAH contaminated sediment<sup>32</sup>, each of these SQGs having its own advantages and limitations. A major difficulty is the assessment of effects of complex mixtures of contaminants, keeping in mind that PAHs normally occur in sediments as a complex mixture. The potential toxic effects of the studied sediments were evaluated using the consensus guideline proposed by Swartz<sup>31</sup>. This guideline provides a unifying synthesis of other SQGs and distinguishes threshold (TEC), median (MEC) and extreme (EEC) effects concentrations. The guideline uses the sum of 13 PAHs (the LMW PAHs naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene and the HMW PAHs fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene). PAH concentrations were normalized to an organic carbon (OC) basis and expressed in  $\mu\text{g g}^{-1}$  OC to adjust for the effect of OC on the PAH partitioning and bioavailability. PAH concentrations in Helkijn and Wervik sediments are between 150 and 395  $\mu\text{g g}^{-1}$  OC and 218 and 551  $\mu\text{g g}^{-1}$  OC, respectively. Most of these concentrations fall within the 95% confidence limits of the TEC (119 – 461  $\mu\text{g g}^{-1}$  OC)

indicating that sediments are unlikely to cause adverse effects on benthic biota. PAH levels in Espierre are higher, ranging from 1130 to 2475  $\mu\text{g g}^{-1}$  OC, and are within the MEC 95% confidence limits (682 – 2854  $\mu\text{g g}^{-1}$  OC), implying that adverse effects might occur.

### 3.3.2 Source apportionment

Sources of the PAH contamination in sediments (pyrolytic or petrogenic) have been investigated by studying the general fingerprint and by using several PAH diagnostic ratios.<sup>33</sup> Samples from the three cores presented here show a predominance of tri- and tetra-ring PAHs. Together tri- and tetra-ring PAHs account for 73-82 % of the total parent PAHs, whereas di-, penta- and hexa-ring PAHs respectively represent 5-10, 7-18 and 3-6 % of the total PAHs. Major non-alkylated PAHs are the tri-ring fluorene and phenanthrene that derive more commonly from petrogenic sources and the tetra- ring fluoranthene and pyrene that derive more commonly from pyrolytic process.

Petrogenic and natural organic matter sources of PAHs are dominated by low molecular weight PAHs (LMW: 2 and 3 aromatic rings) while combustion derived PAHs are predominantly of high molecular weight (HMW: 4, 5 and 6 aromatic rings).<sup>8,34</sup> The ratio of LMW PAHs to HMW PAHs (LMW/HMW) has thus been used to distinguish between petrogenic (>1 values) and pyrolytic (<1 values) origins.<sup>35</sup> The ratio LMW/HMW is around 0.50 for Wervik (mean value 0.58) and Espierre (mean value 0.49) sediments (Fig. 3). Helkijn sediments have LMW/HMW values of about 1 in surface sediments (Fig. 3) suggesting less pyrolytic contaminant and relatively higher inputs of petrogenic PAHs in the Scheldt canal, which is submitted to intense fluvial traffic.

Molecular ratios, based on differences of thermodynamic stabilities between isomers of the same molecular mass, have been frequently used to discriminate between PAH sources.<sup>33</sup> But great care must be taken when applying these ratios for source apportionment in sediments because their use as tracers assumes that isomers have similar physical chemical properties and are subjected to degradation and dilution in the same extent during transport to sediment.<sup>36</sup> Zhang *et al.*<sup>36</sup> demonstrated greater stability of HMW PAH diagnostic ratios compared with LMW PAH ratios which are more influenced by parameters such as volatility. Since PAHs in sediment samples arise from numerous sources, isomer ratios are often studied simultaneously (multiple lines of evidence) in order to avoid misinterpretations.<sup>10,33,34,37</sup> PAH source characterization was examined using the PAHs of molecular mass 178, 202, 228 and 276. Boundary values indicating differences in source type were based on Yunker *et al.*<sup>33</sup> and references therein. The anthracene / (anthracene plus phenanthrene) (A/178) ratio indicates a

petrogenic origin when values are below 0.10 while values  $> 0.10$  are characteristic of combustion derived PAHs. A/178 ratio is often plotted against the fluoranthene / (fluoranthene plus pyrene) ratio (Fl/202).<sup>10</sup> Yunker *et al.*<sup>33</sup> estimates that the boundary value is less definitive for Fl/202 compared with A/178 and conclude that ratios between 0.40 and 0.50 indicate liquid fossil fuel combustion, ratios  $< 0.40$  uncombusted petroleum, and ratios  $> 0.50$  indicate grass, wood, or coal combustion. The benz[a]anthracene / (benz[a]anthracene plus chrysene and triphenylene) (BaA/228) ratio  $< 0.20$  indicates petroleum, values between 0.20 and 0.35 either petroleum or combustion sources, and values  $> 0.35$  combustion. The indeno[1,2,3-*cd*]pyrene / (indeno[1,2,3-*cd*]pyrene plus benzo[ghi]perylene) (IdP/IdP + Bper) ratio  $< 0.20$  indicates petroleum, values between 0.20 and 0.50 liquid fossil fuel combustion and values  $> 0.50$  grass, wood and coal combustion.<sup>33</sup> Zhang *et al.*<sup>36</sup> considers the HMW PAHs indeno[1,2,3-*cd*]pyrene and benzo[ghi]perylene as one of the most reliable PAHs for source apportionment in various media. This is in agreement with Yunker *et al.*<sup>33</sup> who concluded that the 202 and 276 molecular weight ratios lead to more definitive interpretations because of higher differences in thermodynamic stabilities between isomers.

Minimum and maximum values of the isomer diagnostic ratios A/178, BaA/228 and IdP/IdP + Bper are plotted against Fl/202 for each sediment core in Fig. 4. In addition, source ratios of selected standard reference materials (SRMs) were calculated from the certificate of analysis of the National Institute of Standards and Technology: diesel particulate matter SRM 1650, coal tar SRM 1597 and urban dust SRM 1649a. The molecular fingerprints in the core are consistent with a predominant pyrolytic origin of PAHs and are most similar to the coal tar SRM followed by the urban dust SRM (Fig. 4). Samples within each core are very homogeneous in terms of source ratios, indicating little temporal variation at each site. The core with the strongest pyrolytic fingerprint is Espierre, which also has the highest PAH concentrations (Fig. 3 and Fig. 4). A likely source of PAHs in this urbanized area is coal combustion that reaches sediments by atmospheric deposition and runoff from urban areas. Petrogenic sources appear to be minor, with the possible exception of Helkijn where the LMW/HMW ratio is above 1 in surface sediments.

#### 4. Conclusion

The Espierre Canal appeared to be the most contaminated of our sampling sites for both PAHs and biodegraded petroleum residues (UCM). The study of metallic contaminants, which was carried out in sediment cores from the same sites by Lesven *et al.*<sup>7</sup>, also concluded that Espierre sediments were the most contaminated especially in cadmium, lead and zinc. This

high contamination level in the Espierre Canal is maybe the result of former industrial and urban waste water exhausts and of the high population density in this area. PAH contamination levels observed in Espierre sediments ( $40 - 96 \text{ mg kg}^{-1}$ ) were close to those found in France in the Moselle river which also flows through a highly industrialized area<sup>19</sup> and are higher than those typically found in lakes in dense urban settings in the United States.<sup>38</sup> According to sediment quality guidelines, such PAH concentrations might cause adverse effects to the aquatic biota. PAH contamination levels in sediments from the Lys canal ( $6.4 - 11.7 \text{ mg kg}^{-1}$ ) and from the Scheldt ( $4.9 - 8.3 \text{ mg kg}^{-1}$ ) were closer to those measured in the Seine estuary.<sup>39</sup>

The PAH assemblage in all three cores was dominated by fluoranthene and pyrene and in general by high molecular weight compounds (4 to 6 aromatic rings). Fluoranthene and pyrene were also the major PAHs in sediments collected in December 1993 in the Scheldt estuary.<sup>3</sup> This prevalence of combustion-derived PAHs was confirmed in the studied sediments by isomer ratios IdP/IdP + Bper ( $>0.5$ ), BaA/228 ( $>0.1$ ), A/178 ( $>0.2$ ) and Fl/202 ( $>0.5$ ) and is consistent with Van Zoest & Van Eck<sup>2</sup> who concluded that the main source of PAHs in the Scheldt estuary was coal combustion.

Aliphatic hydrocarbons in the studied sediments originate from mixed sources. The anthropogenic origin is evidenced by the presence of a high UCM and by the predominance of petrogenic inputs for low molecular weight *n*-alkanes for Espierre and Helkijn sediments. Biogenic *n*-alkanes of terrestrial origin are predominant for high molecular weight *n*-alkanes in all studied sediments. Wervik sediments distinguish by the higher *n*-alkane concentrations and the predominance of aquatic biogenic hydrocarbons for low molecular weight *n*-alkanes. Espierre site has the higher values of the UCM / R index, the lower values of the *n*-C18 / Phy index and the lower *n*-alkane concentrations, probably as a result of a more important biodegradation of aliphatic hydrocarbons occurring in Espierre sediments.

Based on hydromorphological, biological and physico-chemical quality criteria, the Espierre Canal, the Lys and the Scheldt Rivers are at risk of failing to achieve good ecological potential in 2015.<sup>40</sup> Moreover, dredging to restore navigation in the Espierre Canal is currently underway within the framework of the Blue Links project, partly-financed by the European Union. This study thus provides useful information on the hydrocarbon contamination levels, especially in Espierre sediments, for guiding the disposal of dredging material. Further researches will be undertaken in the Upper Scheldt in order to confirm the results obtained in the three sediment cores and better evaluate the impact of the sediment contamination on water quality

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## Captions

### Graphical content entry

The PAH and *n*-alkane contamination has been evaluated in three sediment cores from the Scheldt River Basin. Here is an aerial photography of the sampling site Wervik (Lys River) which is subjected to several anthropogenic pressures (industrial, recreational and residential areas, navigation, water treatment plant).

### Figure 1

Location of the sampling sites: (1) Espierre (Espierre Canal), (2) Helkijn (Scheldt River), (3) Wervik (Lys River)

### Figure 2

Sedimentary depth profiles in the three sediment cores of (a) the total *n*-alkane concentrations ( $\Sigma$  *n*-alk) in  $\text{mg kg}^{-1}$  and of the aliphatic indexes: (b) CPI (carbon preference index), (c) LCPI (low range carbon preference index), (d) HCPI (high range carbon preference index), (e) UCM/R (unresolved complex mixture / resolved compounds) and (f) *n*-C18/Phy (*n*-C18 / phytane).

### Figure 3

Sedimentary depth profiles of the total PAH concentrations ( $\Sigma$  PAHs) in  $\text{mg kg}^{-1}$  ((a)Wervik and Helkijn cores and (b) Espierre core) and (c) the ratio of low molecular weight PAHs on high molecular weight PAHs (LMW / HMW) in the three sediment cores.

### Figure 4

PAH isomer pair ratios of reference materials and of sediments for the three sites (minimum and maximum values). The ratio Fl / 202 is plotted against the ratios (a) A / 178, (b) BaA / 228 and (c) IdP / IdP + Bper. The graphic representation is based on Oros & Ross<sup>37</sup>.

### Table 1

Sediment properties for the three cores; organic carbon in %, grain size distribution in % of clay (0-4 $\mu\text{m}$ ), silt (4-63 $\mu\text{m}$ ) and sand (63-2000 $\mu\text{m}$ ) and median grain size in  $\mu\text{m}$ .

Table 1

		% OC	% Clay	% Silt	% Sand	d50/ $\mu\text{m}$
Espierre <sup>a</sup>	min	2.4	4.7	46.0	30.2	34.4
	max	4.7	7.1	63.1	48.6	60.4
	med	3.7	5.9	50.5	43.9	51.0
	mean	3.5	5.9	53.5	40.6	48.4
	SD	0.8	0.7	5.7	6.1	8.7
Helkijn <sup>b</sup>	min	1.7	3.5	54.3	11.3	20.3
	max	3.1	9.0	80.4	42.0	52.7
	med	2.1	5.7	72.8	20.1	27.8
	mean	2.5	6.0	70.6	23.4	31.2
	SD	0.7	1.9	8.7	9.6	9.4
Wervik <sup>c</sup>	min	1.5	4.3	50.0	10.4	15.6
	max	3.7	12.0	81.9	43.3	46.3
	med	2.3	7.6	70.5	21.1	26.1
	mean	2.3	7.6	70.1	22.2	25.6
	SD	0.7	1.8	8.5	9.0	7.3

<sup>a</sup> 11 sediment samples; <sup>b</sup> 12 sediment samples; <sup>c</sup> 14 sediment samples; min = minimum; max = maximum; med = median; SD = standard deviation; OC = organic carbon; d50 = median grain size.