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# Journal Pre-proof

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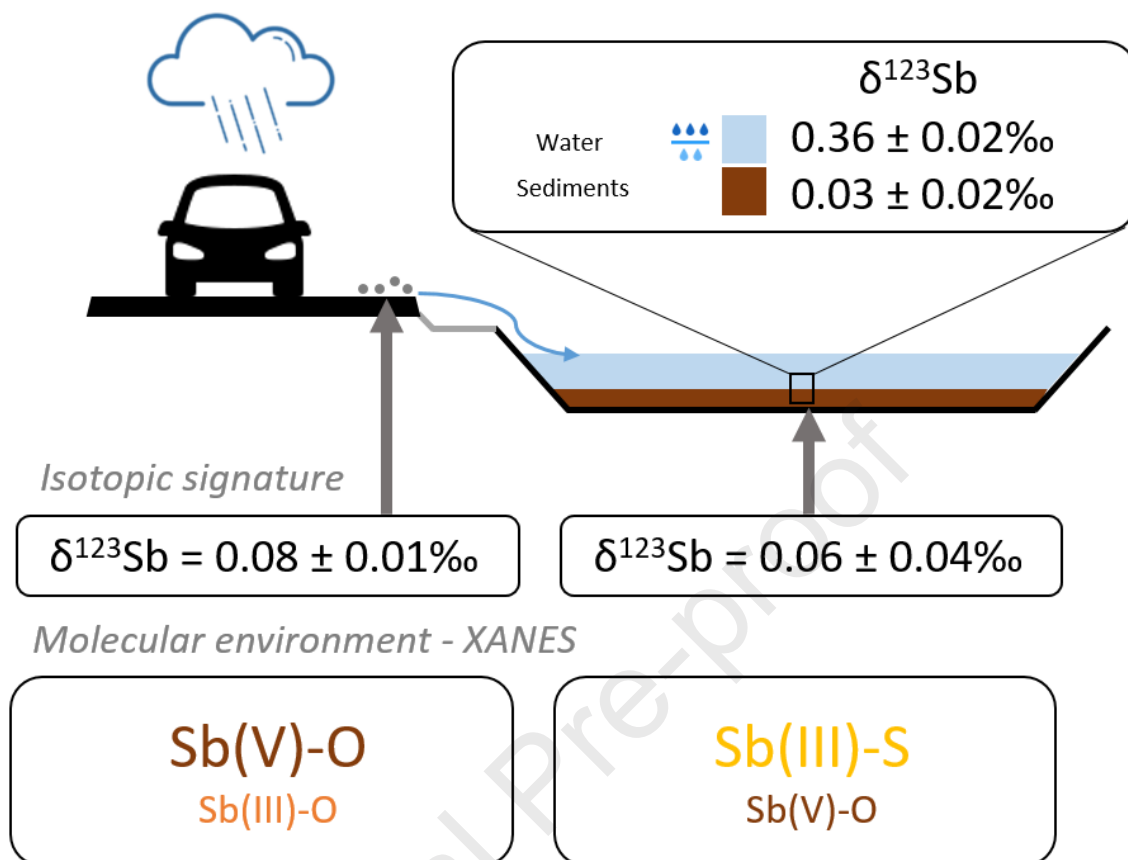
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1 **Fate of antimony contamination generated by road traffic – A focus on Sb geochemistry**  
2 **and speciation in stormwater ponds**

3

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27 **Highlights**

- 28
- Highway stormwater ponds concentrate Sb contamination from road runoff
- 29
- Sb isotopic composition of stormwater pond sediments is close to that of road dusts
- 30
- Sb(V)-O, Sb(III)-O, and Sb(III)-S species occur in the road-to-pond continuum
- 31
- Sb(III)-S species are observed as a specific signature of underwater reduced samples
- 32
- Sb speciation changes along the waterway show the high geochemical reactivity of Sb

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34 **Abstract**

35 Although antimony (Sb) contamination has been documented in urban areas, knowledge gaps  
36 remain concerning the contributions of the different sources to the Sb urban biogeochemical  
37 cycle, including non-exhaust road traffic emissions, urban materials leaching/erosion and  
38 waste incineration. Additionally, details are lacking about Sb chemical forms involved in urban  
39 soils, sediments and water bodies. Here, with the aim to document the fate of metallic  
40 contaminants emitted through non-exhaust traffic emissions in urban aquatic systems, we  
41 studied trace element contamination, with a particular focus on Sb geochemistry, in three  
42 highway stormwater pond systems, standing as models of surface environments receiving  
43 road-water runoff. In all systems, differentiated on the basis of lead isotopic signatures, Sb  
44 shows the higher enrichment factor with respect to the geochemical background, up to 130,  
45 compared to other traffic-related inorganic contaminants (Co, Cr, Ni, Cu, Zn, Cd, Pb).  
46 Measurements of Sb isotopic composition ( $\delta^{123}\text{Sb}$ ) performed on solid samples, including air-  
47 exposed dusts and underwater sediments, show an average signature of  $0.07 \pm 0.05\text{‰}$  ( $n=25$ ,  
48 all sites), close to the  $\delta^{123}\text{Sb}$  value measured previously in certified reference material of road  
49 dust (BCR 723,  $\delta^{123}\text{Sb} = 0.03 \pm 0.05\text{‰}$ ). Moreover, a fractionation of Sb isotopes is observed  
50 between solid and dissolved phases in one sample ( $n=3$  samples), which might result from Sb  
51 (bio)reduction and/or adsorption processes. SEM-EDXS investigations show the presence of  
52 discrete submicrometric particles concentrating Sb in all the systems, interpreted as friction  
53 residues of Sb-containing brake pads. Sb solid speciation determined by linear combination  
54 fitting of X-Ray Absorption Near Edge Structure (XANES) spectra at the Sb *K*-edge shows an  
55 important spatial variability in the ponds, with Sb chemical forms likely driven by local redox  
56 conditions: “dry” samples exposed to air exhibited contributions from Sb(V)-O (44% to 100%)  
57 and Sb(III)-O (<10% to 56%) species whereas only underwater samples, representative of  
58 suboxic/anoxic conditions, showed an additional contribution from Sb(III)-S (48% to 81%)  
59 species. Altogether, these results confirm the traffic emission as a specific source of Sb  
60 emission in surface environments. The spatial variations of Sb speciation observed likely

61 reflect an important geochemical reactivity in this context, which could have important  
62 implications on Sb transfer properties in (sub)surface hydrosystems.

63

64 **Keywords:** antimony, road traffic contamination, stormwater ponds, Sb isotopes, Sb  
65 speciation, Pb isotopes.

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## 67 1. Introduction

68 Global-scale antimony (Sb) contamination has been recorded in ice cores since the  
69 early 1900s (Krachler et al., 2005; Liu et al., 2021). In particular, the increase in Sb  
70 concentrations has been interpreted as a rise of anthropogenic inputs related to waste  
71 incineration and mining (Krachler et al., 2005; Liu et al., 2021). At the urban scale, different  
72 sources contribute to the Sb biogeochemical cycle, including non-exhaust road traffic  
73 emissions, urban materials leaching/erosion and waste incineration (Filella et al., 2009). In the  
74 urban Orge River basin (Paris region, France), an increase in Sb enrichment factors in river  
75 suspended particulate matters (SPM) has been persistently observed along the increasing  
76 urbanization gradient (Le Pape et al., 2012; Froger et al., 2018). In Budapest (Hungary), Sb  
77 atmospheric contamination has been observed in urban aerosols, showing extreme  
78 enrichment factors, from 5,097 in PM<sub>10</sub> to 18,892 in PM<sub>2</sub>, and were interpreted as resulting  
79 from road traffic (Salma and Maenhaut, 2006). Indeed, road traffic is known to induce  
80 emissions of inorganic contaminants due for instance to abrasion of brake pads (Von Uexküll  
81 et al., 2005; Napier et al., 2008; Hu et al., 2017), namely copper (Cu), zinc (Zn), cadmium (Cd),  
82 chromium (Cr) and Sb. In particular, Sb has been used in brake pads lubricants (Sb<sub>2</sub>S<sub>3</sub>) as  
83 replacement for asbestos (Chan and Stachowiak, 2004; Lee et al., 2013). Additionally, metallic  
84 trace element emissions are also reported as originating from tires and oils combustion or  
85 leakage (Hjortenkrans et al., 2007; Davis et al., 2001; Johansson et al., 2009) and other urban  
86 materials such as safety barriers, road paints or cigarette butts (Zhang et al., 2004; Moriwaki  
87 et al., 2009; Kibblewhite, 2018; Turner and Filella, 2020). After their emission at the road scale,  
88 these contaminants are transported by road runoff and potentially impact the quality of surface  
89 waters (Helmreich et al., 2010; Le Pape et al., 2012; Wang et al., 2017; Froger et al., 2018).  
90 Although traffic is generally mentioned as a major source of Sb in the urban environment  
91 (Hjortenkrans et al., 2006; Johansson et al., 2009), its contribution to the global urban Sb  
92 contamination is poorly quantified. Nonetheless, identification of the contributions of the  
93 diverse sources and pathways of Sb contamination could lead to a better management of this

94 pervasive and persistent geochemical enrichment, for instance by adapting public policy to  
95 control or remove part of these contamination sources.

96 Highway stormwater ponds, located along roads, are recognized as efficient accumulators  
97 of road contaminations since they directly receive the runoff water leaching roads and other  
98 surfaces contaminated by vehicles-related emissions (Hares and Ward, 1999; Clozel et al.,  
99 2006; Hwang et al., 2016). Additionally, as some of these stormwater pond systems are  
100 vegetated, and harbour sedimentary systems representative of urban soils and sediments,  
101 they stand as interesting model hydrosystems (Stachel et al., 2010) to study the mechanism  
102 of Sb accumulation from road emissions. While Cu, Zn, Cd, Cr and Pb concentrations from  
103 measurements in road and street dusts are often reported in the literature (e.g. Ahmed and  
104 Ishiga, 2006; Haus et al., 2007), Sb enrichment and chemistry have rarely been studied in  
105 road-related environments, in particular in such stormwater pond systems. A few data are  
106 currently available for road ponds, and only focusing on Sb contamination level based on the  
107 measurements of its concentrations in bulk and dissolved fraction of pond water samples from  
108 Germany, England, Sweden and Canada (up to  $11 \mu\text{g}\cdot\text{L}^{-1}$  (Kamalakkannan et al., 2004;  
109 Stachel et al., 2010; Nielsen et al., 2015; Perron and Pick, 2020)) and in sediments from a UK  
110 motorway drainage pond ( $1.44 - 2.01 \text{ mg}\cdot\text{kg}^{-1}$ ) (Kamalakkannan et al., 2004). However, neither  
111 speciation nor isotopic measurements are currently available on these accumulating pond  
112 system media, data which could be extended to surface media exposed to road emissions  
113 such as urban areas in general.

114 To study the sources and the transfer pathways of contaminant-bearing particles, the  
115 relative abundance in contaminant isotopes in both the aqueous and the solid phases has  
116 proven to be an informative geochemical parameter (Monna et al., 1997). For instance, in  
117 urban context,  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios have been used as anthropogenic source  
118 tracers in soils (Emmanuel and Erel, 2002), or to estimate the urban pressure exerted on urban  
119 rivers (Ayrault et al., 2012; Le Pape et al., 2013). Indeed, Pb is a common and abundant  
120 contaminant of urban environments, whose isotopic composition allows discriminating

121 between natural and anthropogenic sources for lead-bearing particles (Ayrault et al., 2012).  
122 Comparatively, Sb isotopic signature has been scarcely used in the literature, and has never  
123 been used to trace Sb contamination in the urban context. The pioneering study of Rouxel et  
124 al. (2003) gives the first values of Sb fractionation between  $^{123}\text{Sb}$  and  $^{121}\text{Sb}$  for different natural  
125 samples representative of diverse sources at the Earth surface, including seawater and main  
126 geological rocks. This study also suggests that Sb isotopic fractionation could be a useful tracer  
127 for biogeochemical processes affecting Sb, such as changes in oxidation state. More recently,  
128 in environmental sciences,  $\delta^{123}\text{Sb}$  has been used to trace the contributions from different Sb-  
129 sources in mine-impacted streams (Resongles et al., 2015b). Thus, Sb isotopic signature has  
130 a good potential for both discriminating the sources of Sb at the site scale and could also help  
131 to trace the local biogeochemical processes involving changes of oxidation state, ligand  
132 exchange, or adsorption onto natural particles (Ferrari et al., 2022; Zhou et al., 2022).

133 Determining the physico-chemical processes governing Sb mobility in surface  
134 environments is essential to unravel the transfer pathways leading to the dissemination of this  
135 toxic metalloid. As Sb is a redox sensitive element, Sb mobility is strongly driven by its  
136 speciation in both the aqueous and the solid phases. In (sub-)surface soils and sediments, Sb  
137 harbours two oxidation states, Sb(III) and Sb(V), the latter form presenting the higher solubility  
138 (Johnston et al., 2020). Thus, determining Sb speciation is of prime importance to predict Sb  
139 short- to long- term transfer properties. Currently, the few information on Sb speciation have  
140 been obtained *via* chemical extractive methods applied to road soils, road dusts, and airborne  
141 particles (Amereih et al., 2005; Quiroz et al., 2013; Sánchez-Rodas et al., 2017), showing  
142 various contributions from both Sb(III) and Sb(V) species. Varrica et al. (2013) have measured  
143 Sb speciation *via* X-ray Absorption Spectroscopy (XAS) at the Sb *K*-edge in various urban  
144 particles, and observed a mix of Sb(V)-O, Sb(III)-O and Sb(III)-S molecular environments,  
145 interpreted as directly resulting from brake pad friction and abrasion (Cho et al., 2006; Martinez  
146 and Echeberria, 2016). Thus, a full comprehensive description of Sb speciation along the road-  
147 to-pond continuum is necessary to determine whether Sb speciation is inherited from direct

148 traffic inputs or can be further influenced by local biogeochemical processes taking place in  
149 surface soils and sediments.

150 Here, we have compared the level of trace metal contamination, including Sb, in three  
151 stormwater pond systems along roads presenting high traffic volumes in the Ile-de-France  
152 region (France). These sites are taken as model systems representative of surface  
153 environment accumulating the contaminations from road traffic, which can be largely found in  
154 urban areas (e.g. urban hydrosystems, rivers, wetlands). Additionally, the studied sites are  
155 representative of different land uses (rural and urban) and of different chronologies of dust and  
156 sediment deposition. Both sediments and waters were sampled in the road-to-pond continuum,  
157 with the aim to reveal the spatial evolution of trace element contamination from emission to  
158 deposition in near road environments. Thanks to a combination of techniques, including  
159 contaminant concentration analyses (among them Cu, Cd, Cr, Ni, Pb, Sb, Zn), analysis of  
160 relative abundance of Pb and Sb isotopes, and speciation analysis of Sb, we highlight key  
161 steps of Sb biogeochemical cycle in surface environments impacted by road traffic. Thus, we  
162 show that the level and type of contamination of pond systems is likely related to the nature of  
163 drained surfaces (urban vs. rural) and extent of particle accumulation. Then, we identified a  
164 specific  $\delta^{123}\text{Sb}$  signature of highway stormwater pond samples, including road dusts and  
165 sediments, which is shown to be close of that reported elsewhere for road dust. Finally, we  
166 studied in detail the variations of Sb speciation by the mean of XANES at the Sb *K*-edge in  
167 solid samples along the road-to-pond continuum, showing that Sb presents an important  
168 geochemical reactivity, with multiple oxidation states and ligands involved as a function of the  
169 local redox conditions.

## 170 **2. Materials and methods**

### 171 **2.1. Study sites**

172 The three highway stormwater pond systems studied are located in the south of Île-de-  
173 France region in the Orge River watershed (Fig. SI-1.1). Previous researches performed in the  
174 Orge River basin have provided a good knowledge of land use, geology, spatial and temporal

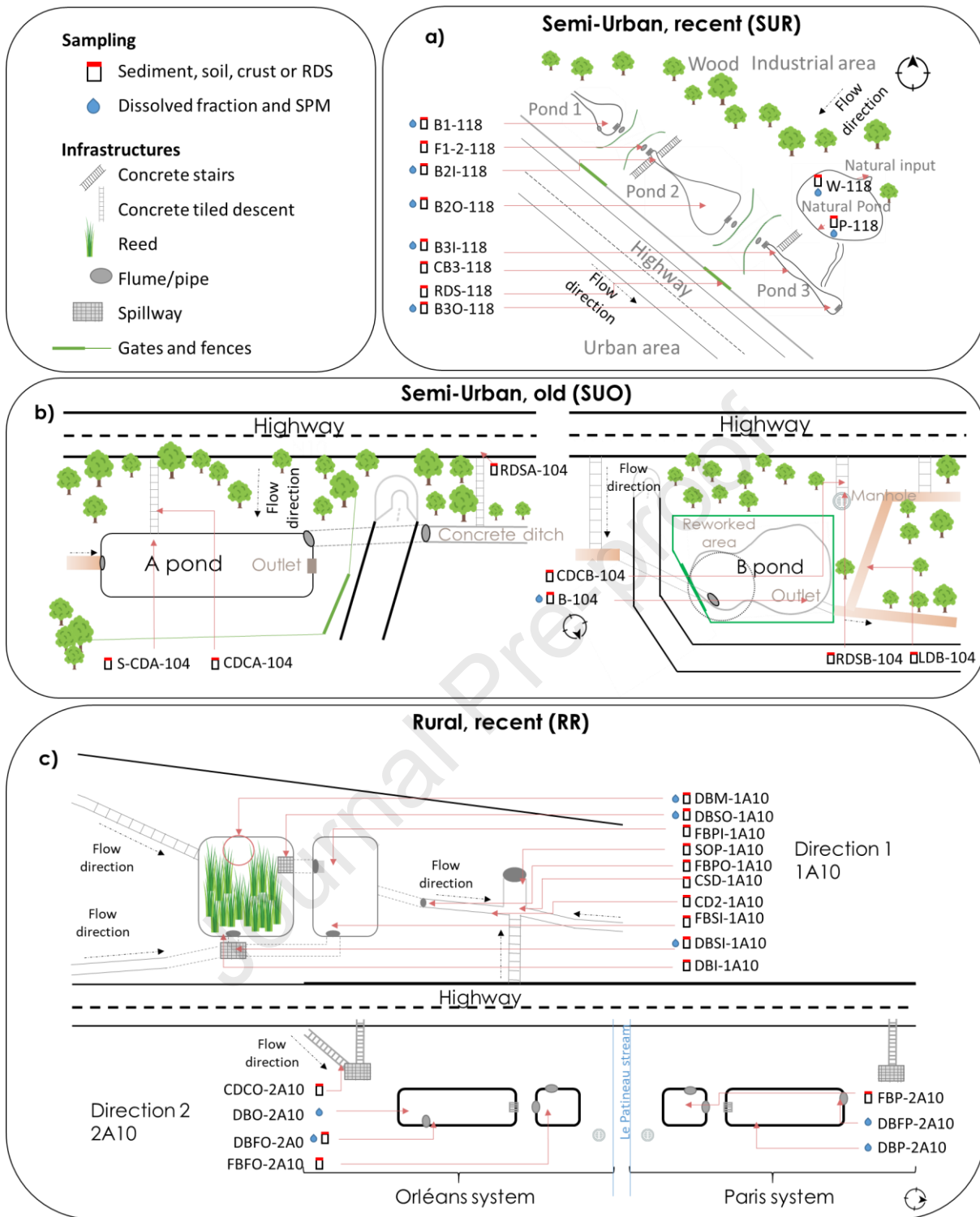
175 dynamics of contaminants of anthropogenic origin (e.g. metals and PAHs) (Le Pape et al.,  
176 2012; Froger et al., 2018, 2019). The highway stormwater pond systems studied are different  
177 by the nature of drained areas (urban + road, mostly road or 100% road) but also by their  
178 design (decantation pond, filtration pond, presence or not of a polyethylene geomembrane)  
179 and their construction date (Table 1). Road sections related to the studied stormwater ponds  
180 have a high daily flux of ~50000 vehicles per day (Table 1). The presence of speed cameras  
181 near both semi-urban systems should be noted because it induces braking and therefore the  
182 emission of dust due to abrasion of brake pads. Three systems are studied: recent semi-urban  
183 (SUR) situated in Orsay, old semi-urban (SUO) situated in Marcoussis, and recent rural (RR)  
184 situated near Saint-Martin-de-Bréthencourt. Figure 1 represents the spatial organization of the  
185 three stormwater pond systems. The SUR system is composed by 3 geomembrane isolated  
186 ponds arranged in series and connected by rafts at their base and by nozzles in height for  
187 overflows during important rain events. The first pond (B1) is located upstream and the third  
188 (B3) downstream. Both B1 and B2 are planted with reeds while B3 is channeled and unplanted.  
189 A “natural pond” (P) supplied by the upperlying aquifer of the Fontainebleau sands (W),  
190 independent of the road runoff collection network but hydrologically connected to B3, is also  
191 present. The SUO system is composed by 2 disconnected unplanted decantation ponds  
192 situated in an urban area surrounded by crops. The “A” pond had been dredged a few days  
193 before sampling while “B” pond has never been dredged since the pond construction (Figure  
194 1). The RR system is divided in two sub-sites: “Direction 1” (1A10) composed by a  
195 geomembrane isolated decantation pond planted with reeds in series with a dry filtration pond  
196 and “Direction 2” (2A10) composed by two systems of unplanted geomembrane isolated  
197 decantation ponds in series with dry filtration ponds. Waters from both sub-sites come from  
198 the road through a spillway system.

## 199 **2.2. Sampling**

200 Sediments (S), concrete downhill crusts (CDC), road dust sediments (RDS), water samples  
201 (dissolved fraction (W) and suspended particulate matters (P)) were sampled during the five

202 sampling campaigns carried out in January (2 campaigns) and February 2020 for SUR and  
203 SUO systems and March and September 2020 for the RR system.

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205 **Figure 1.** Layout of the three studied stormwater ponds systems. (a) Semi-Urban Recent  
 206 system (SUR) of Orsay, (b) Semi-Urban Old system (SUO) of Marcoussis and (c) Rural Recent  
 207 system (RR) of Saint-Martin-de-Bréthencourt. Sampling locations for each type of samples  
 208 (water, SPM, sediment) are indicated on the schemes. Pots symbols stand for solid sampling,  
 209 drops stand for water sampling (dissolved phase, <math><0.22 \mu\text{m}</math>) and suspended particulate  
 210 matters (SPM > 0.3  $\mu\text{m}</math>) sampling.$

211

212 **Table 1.** Characteristics of the highway stormwater pond systems (year of construction, type  
 213 of pond conception, type of drained surfaces, traffic intensity and presence of speed cameras)

Denomination	GPS coordinates	Construction (year)	Type	Drained surface	Traffic per day (2017)	Presence of speed camera
<b>Semi-urban, recent (SUR)</b>	48.7115, 2.1863	~2000	Decantation	Urban + Road	54,187	Yes
<b>Semi-urban, old (SUO)</b>	48.6334, 2.2246	1990s	Decantation	Road	56,595	Yes
	48.6320, 2.2292					
<b>Rural, recent (RR)</b>	48.5120, 1.9072	2012	Decantation + filtration	Road	42,225	No
	48.5125, 1.9082					

214

215 Underwater sediments were collected in 180 mL polypropylene containers tightly closed  
 216 onsite and a water column was kept above the sediments to avoid direct contact with air. Such  
 217 reduced sediments were then inserted as quickly as possible in a glove box at the IMPMC  
 218 laboratory for further sample processing. Inside the glove box, the solid samples were  
 219 separated from the liquid phase by centrifugation, dried under vacuum, and finally stored in  
 220 anoxic conditions (N<sub>2</sub>, <5 ppm O<sub>2</sub>). Dissolved fraction of the water samples was recovered by  
 221 filtering to 0.22 µm with PES filters (Sartorius Minisart™) and acidified with ultrapure nitric acid  
 222 (0.5 M) in 50 mL Falcon® tubes directly on site and further stored at 4 °C. Bulk water (~ 2 L)  
 223 was collected in PET bottles previously washed with HNO<sub>3</sub> 0.5 N and rinsed on site with bulk  
 224 water. Water pH, conductivity and temperature were measured onsite except for 2 samples in  
 225 the RR pond system (15 water samples listed in Table SI-1.2). Road dust sediments (RDS)  
 226 were collected on the road using a plastic spatula and placed in a tightly closed polyethylene  
 227 bag (SUO system) or using a plastic brush and kept in a Falcon tube® (SUR system). Crusts  
 228 were collected on the slope concrete tiles channeling water from the road to the pond with a  
 229 plastic spatula and kept in a tightly closed polyethylene bag. RDS and crusts were stored at  
 230 room temperature in the dark. Full information about the 41 solid samples (conditions of  
 231 sampling, drying conditions, type and matrix) are listed in Table SI-1.1.



## 2.3. Sample preparation

### 2.3.1. Suspended particulate matter (SPM) and sediment

Within the hours following collection, SPM samples were obtained by filtration (in laboratory) of approximately 2 L of bulk water (sometime less when clogging occurred) through previously dried and weighted quartz filters (Pallflex® Tissuquartz™, retaining 99.9% of >0.3 µm particles) using glass or plastic tulips previously rinsed with 0.5 N nitric acid and a pump. The filtered volume was measured by weighting. After filtration, filters were dried under oxic conditions before total mineralization (Priadi et al., 2011). For multi-elemental analysis, approximately 100 mg of sediment, previously sieved at 2 mm with a plastic sieve, were crushed in an agate mortar before total mineralization (Le Pape et al., 2012).

### 2.3.2. Bulk mineralization

Total digestion of sediments and SPM was performed in three steps using ultrapure concentrated acids to avoid contaminations in open PTFE Savillex® vials: 4 mL of HF (47-51%) and 2 mL HClO<sub>4</sub> (67%) heated at 150 °C for 320 minutes, 3.75 mL of HCl (34-37%) and 1.25 mL of HNO<sub>3</sub> (67%) heated at 120°C for 180 minutes and finally heating at 110 °C with addition of 1 mL of HNO<sub>3</sub> (67%) for 55 minutes. Final solutions were transferred to 50 mL Falcon® (polyethylene) tubes, Savillex® vials rinsed three times by heating approximately 10 mL of HNO<sub>3</sub> 0.5 M and completed at 50 mL with 0.5 M nitric acid (Le Pape et al., 2012). Two certified reference materials (CRM), sediment SL1 and street dust BCR 723, were added in each mineralization batch. Blanks were performed in each batch and a filter blank was included in each SPM batches.

## 2.4. Analytical methods

### 2.4.1. Elemental analysis and enrichment factors calculation

The concentrations of 25 major, minor and trace elements were determined using triple quadrupole inductively coupled plasma – mass spectrometry (TQ-ICP-MS) (Thermo Scientific™ iCAP™ TQ) at LSCE laboratory (Tables SI-1.3, SI-1.4, SI-1.5). An internal

258 standard mixture (In, Ge, Rh and Re) was added on-line to the samples to correct for the  
 259 instrumental sensitivity drift. Quality of analysis was checked using NIST 1640a (spring water)  
 260 for dissolved samples, SL1 and BCR-723 for sediments (100 mg) and for SPM (10 mg) (Table  
 261 SI-1.6). Accuracy was within  $\pm 15\%$  of the certified values provided for the certified reference  
 262 material SL1 and BCR 723 (except Ag: 19%). The RSD for SPM are higher ( $< 32\%$ ): measured  
 263 concentrations were close to quantification limits due to the low mass of SPM recovered on  
 264 filters.

265 Enrichment Factors (EF) are classically used to determine the contamination level of solid  
 266 samples (Salma and Maenhaut, 2006; Le Pape et al., 2012; Froger et al., 2018). EFs are  
 267 calculated as a comparison of the Al-normalized trace element concentration in the sample  
 268 with the local background values (Equation 1).

$$269 \quad EF = \frac{\frac{X_{\text{Sample}}}{Al_{\text{Sample}}}}{\frac{X_{\text{Background}}}{Al_{\text{Background}}}} \quad (1)$$

270 with  $X_{\text{Sample}}$  and  $X_{\text{Background}}$  the concentrations of the element under consideration in the sample  
 271 and its geochemical background, and  $Al_{\text{Sample}}$  and  $Al_{\text{Background}}$  the aluminum concentrations in  
 272 the sample and in the geochemical background. Local background determined for the Orge  
 273 River catchment for Sb by (Froger et al., 2018) and for the Seine River for Al, Cd, Cr, Cu, Ni,  
 274 Pb and Zn by (Thévenot et al., 2007) were used to calculate the EFs. Full set of elemental  
 275 concentrations and associated EFs are shown in Table SI-1.7. Details on the use and  
 276 calculations of enrichment factors according to the interpretation of Sutherland (2000) are  
 277 given in the supplement information section.

#### 278 **2.4.2. Radiogenic lead isotope ratio analysis**

279 Radiogenic lead isotopic ratios ( $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$ ) were measured by TQ-  
 280 ICP-MS in solid samples previously mineralized and diluted to obtain a Pb concentration of 2  
 281  $\mu\text{g.L}^{-1}$  in solution. In order to control mass bias and/or instrument drift, an isotopic Pb reference  
 282 material, NIST NBS 981, was measured every two samples. To control measurement

283 accuracy, a mineralized lake sediment reference material SL1 was measured multiple times  
284 with the samples and the results were compared to the data  $1.217 \pm 0.008$  in  $^{206}\text{Pb}/^{207}\text{Pb}$  and  
285  $2.037 \pm 0.003$  in  $^{208}\text{Pb}/^{206}\text{Pb}$  published by Farmer et al. (2002), our SL1 measurements are in  
286 the margins of errors. The method is more detailed in Supplementary information (SI-3) and  
287 the results are shown in Table SI-1.8. In this study, lead isotope ratio signature was used as  
288 tracer for contaminant sources to study the nature of sediment inputs in each pond system  
289 (Komárek et al., 2008) using the published isotopic signature of the potential local sources of  
290 Pb (Figure SI-3.1; Table SI-1.8), *i.e.* the local urban Pb endmember, the local Pb geochemical  
291 background, and the French leaded gasoline.

### 292 **2.4.3. Antimony isotopic composition analysis**

293 An aliquot of water samples and mineralized solutions of solid samples containing  
294 50-100 ng of Sb underwent a purification step on TSP cartridges (thiol-functionalized  
295 mesoporous silica powder) in order to separate Sb from the other chemical species and to  
296 preconcentrate it in low-concentrated samples according to the method detailed in Ferrari et  
297 al. (2021). For each batch of purification, a certified reference material (BCR 723, Table SI-  
298 1.9) and a blank was included. Blanks contribution represented less than 0.8 ng de Sb (<1.6%).  
299 Antimony isotopic composition of the samples were then analysed by HG-MC-ICP-MS  
300 (Hydride Generation coupled to a Multi-Collector Inductive Coupled Plasma Mass  
301 Spectrometer, Neptune+, Thermo Fisher Scientific) on the AETE-ISO platform (OSU OREME,  
302 University of Montpellier), using instrument parameter settings given in Ferrari et al. (2021). A  
303 sample-standard bracketing approach was used to correct the mass bias. An in-house isotopic  
304 Sb standard solution (SPEX CertiPrep (Sb  $1,000 \mu\text{g mL}^{-1}$  in 20% w/w HCl, batch number 24-  
305 175SBX)) was analysed before and after every sample. The isotopic composition of Sb was  
306 expressed according to equation 2 which represents the deviation between the isotope ratio  
307 measured for the sample and the mean isotope ratio of the in-house isotopic standard (SPEX)  
308 measured before and after the sample. Detailed results are presented in Table SI-1.9.

$$\delta^{123}\text{Sb}(\text{‰}) = \left( \frac{\left( \frac{^{123}\text{Sb}}{^{121}\text{Sb}} \right)_{\text{sample}} - \left( \frac{^{123}\text{Sb}}{^{121}\text{Sb}} \right)_{\text{mean std}}}{\left( \frac{^{123}\text{Sb}}{^{121}\text{Sb}} \right)_{\text{mean std}}} \right) \times 1000 \quad (2)$$

310 Antimony isotopes could help in determining the transfer pathways of Sb contamination  
 311 by tracing the contributions of distinct sources (Rouxel et al., 2003). Sb isotopes data have  
 312 mainly been determined in mine-affected environments and river waters ( $\delta^{123}\text{Sb} = -0.06\text{‰}$  to  
 313  $+0.83\text{‰}$ ) (Resongles et al., 2015a), in environmental references samples (Rouxel et al., 2003;  
 314 Ferrari et al., 2021; Sun et al., 2021; Wang et al., 2021), and in ancient glass materials (Lobo  
 315 et al., 2013; Degryse et al., 2015; Dillis et al., 2019). Here, this tool is applied for the first time  
 316 to road- affected surface environmental samples in an attempt to trace the contributions of  
 317 distinct Sb sources, which could help in determining the transfer pathways of Sb contamination.

#### 318 **2.4.4. Powder X-ray diffraction (XRD)**

319 Powder XRD diffractograms were collected on a Panalytical™ Xpert pro®  
 320 diffractometer in the Bragg-Brentano geometry using Co  $K\alpha$  radiation to minimize Fe X-ray  
 321 fluorescence. Samples were previously crushed in an agate mortar to obtain a fine powder.  
 322 Bragg reflexions were indexed using the Highscore Plus® software associated to the PDF 2  
 323 database (2020). To check for potential sample oxidation, test samples were first measured  
 324 within an anaerobic chamber and results were compared to those obtained without the  
 325 chamber. As no changes were observed in XRD data for underwater anoxic test samples, the  
 326 whole set of samples was consequently analysed under oxic conditions. Reference  
 327 compounds of ferrihydrite co-precipitated with Sb(V) or Sb(III), synthesized for X-Ray  
 328 absorption measurements at the Sb  $K$ -edge (see supplementary information SI-2 for synthesis  
 329 details), were analysed by X-Ray diffraction and Wide angle X-ray Scattering associated to  
 330 Pair distribution function analysis on the CRISTAL beamline at SOLEIL.

#### 331 **2.4.5. Scanning electron microscopy coupled with energy dispersive X-** 332 **ray spectroscopy (SEM-EDXS)**

333 SEM investigation associated to punctual EDXS analysis was performed on non-  
334 crushed samples embedded in resin to conserve the aggregate structure of particles at the  
335 microscopic scale. SEM-EDXS analyses were performed at IMPMC, with a GEMINI ZEISS™  
336 Ultra55 Field Emission Gun Scanning Electron Microscope equipped with a Bruker™ Si-drift  
337 detector for EDXS acquisition. Prior to analysis, bulk samples were embedded in an epoxy  
338 resin (Epoxy, Presi™) and polished. Polished sections samples were coated with carbon  
339 before SEM observation. EDXS spectra were performed on specific spots on the surface on  
340 samples using the esprit 1.9 or 2.2 software.

#### 341 **2.4.6. X-ray absorption spectroscopy at the Sb K-edge**

342 To examine the potential changes of Sb chemical forms along the road-to-pond  
343 continuum, X-Ray Absorption Spectroscopy Near Edge Structure (XANES) measurements  
344 were performed on the solid samples. Given the large shifts in energy between different types  
345 of molecular environments and ligands at the Sb *K*-edge (typically 4 eV between maxima for  
346 Sb(V)-O and Sb(III)-O, and 2 eV between maxima for Sb(III)-O and Sb(III)-S), XANES  
347 measurements classically allow the quantification of the different species in samples of  
348 unknown speciation, namely the contributions of Sb(V)-O, Sb(III)-O, and Sb(III)-S (Bennett et  
349 al., 2017; Arsic et al., 2018; Burton et al., 2020). Hereafter in the text, in the section concerning  
350 speciation by XANES at the Sb *K*-edge, the samples are labelled as “Dry” when they were  
351 sampled as dried powders on the field and as “Underwater” when they were collected under a  
352 column of water and kept under anoxic conditions until analysis. The single “Wet” sample was  
353 collected as wet and dried at the laboratory under oxic conditions.

##### 354 **2.4.6.1. Synthesis of reference compounds, sample preparation and data** 355 **sampling**

356 Ferrihydrite coprecipitated with Sb(III) and Sb(V) (Fh-Sb(III) or Fh-Sb(V)), tripuhyite  
357 (FeSbO<sub>4</sub>) and amorphous antimony trisulphide (Sb<sub>2</sub>S<sub>3</sub>) were synthesized to serve as reference

358 compounds. Details on the synthesis protocols can be found in the supplement information  
359 section (SI-2).  $\text{Sb}_2\text{O}_3$  was purchased from Sigma Aldrich. For reference compounds, an  
360 appropriate amount of sample was diluted into cellulose and pressed in pellets for transmission  
361 measurement when possible. For Fh-Sb samples, spectra were measured in fluorescence  
362 mode. For environmental samples from stormwater ponds, pure sample pellets were prepared  
363 by pressing approximately 50 mg of finely ground sample in a Jacomex™ glove box ( $\text{O}_2 < 4$   
364 ppm). All pellets were covered with Kapton® tape and transported to the synchrotron facility in  
365 anoxic containers according to proven protocols (e.g. Le Pape et al., 2017).

366 Antimony *K*-edge X-ray absorption spectroscopy data were collected in both  
367 transmission and fluorescence detection modes at 80 K in a liquid azote cryostat on the  
368 bending magnet SAMBA beamline at SOLEIL Synchrotron (Gif-sur-Yvette, France).  
369 Fluorescence signals were measured using a Canberra™ 36-elements Ge array detector and  
370 incoming beam energy was monitored through a Si (220) double-crystal monochromator. Data  
371 were calibrated using a Sb foil at 30,491 eV at the first inflexion point of the first derivative of  
372 the XANES spectrum. Samples were mounted on PEEK sample holders in a Jacomex™ glove  
373 box onsite. Sample holders were immersed in liquid  $\text{N}_2$  for the transfer to the beamline cryostat.  
374 Because Sb concentrations in samples were less than  $100 \text{ mg.kg}^{-1}$ , a minimum of 25 quick  
375 scans were necessary to obtain a good signal to noise ratio for each natural sample.

#### 376 **2.4.6.2. Data processing and analysis**

377 The FASTOSH program (Landrot, 2018) was used to calibrate and normalize Sb *K*-  
378 edge extended X-Ray absorption near edge structure data and to proceed to background  
379 subtraction. A linear combination fitting (LCF) analysis was performed on the XANES spectra  
380 on the first derivative of the absorption to determine the relative contributions of Sb(V)-O,  
381 Sb(III)-O and Sb(III)-S species in the stormwater pond samples. To do so, the Fh-Sb(V), Fh-  
382 Sb(III), and am- $\text{Sb}_2\text{S}_3$  references compounds were considered as the most relevant to perform  
383 the LCF analysis. LCF accuracy on derivative of XANES spectra were estimated by a R-factor  
384 (Equation 3) and reduced chi-square (Equation 4):

385

$$386 \quad R - factor = \frac{\sum_{p=1}^t [data(p) - fit(p)]^2}{\sum_{i=1}^m [data(p)]^2} \quad (3)$$

$$387 \quad \chi_R^2 = \frac{1}{(t-s)} \sum_{i=1}^t [data(i) - fit(i)]^2 \quad (4)$$

388

389 With “data” designating the experimental spectrum, “fit” the spectrum reconstructed by LCF,  
 390 “p” a specific point in each spectrum, “t” the total number of points in each spectrum, “i” an  
 391 independent data point corresponding to a specific independent measurement and “s” the  
 392 number of reference spectra considered in fit.

### 393 **3. Results**

#### 394 **3.1. Radiogenic lead isotope ratios in solid samples**

395 The detailed results of lead isotope ratio analysis are shown in the Supplementary  
 396 information (SI-3). The recent rural stormwater pond system (RR) signatures are distributed  
 397 on a mixing line between the leaded gasoline and the local geochemical background  
 398 endmembers. Lead isotope ratios measured in the SUR and SUO pond system fall on the  
 399 same mixing line but the range of variations is smaller and isotopic signatures are close to the  
 400 urban lead endmember. Extreme value close to the gasoline endmember is measured for the  
 401 S-DBSI-1A10 sample collected at the entry pond spillway, *i.e.* located directly at the entrance  
 402 of the pond system receiving road runoff. The closest value to the geochemical background  
 403 signature is observed for the sediment sample S-P-118, which is located in SUR system  
 404 natural freshwater pool receiving water from the overlaying Fontainebleau sand aquifer.  
 405 Accordingly, this sample presents a particularly low Pb concentration ( $16 \text{ mg.kg}^{-1}$ ), confirming  
 406 that this part of the system is not collecting road traffic runoff.

407

### 3.2. Analysis of highway stormwater pond contamination: spatial variation of elemental geochemistry and enrichment factors

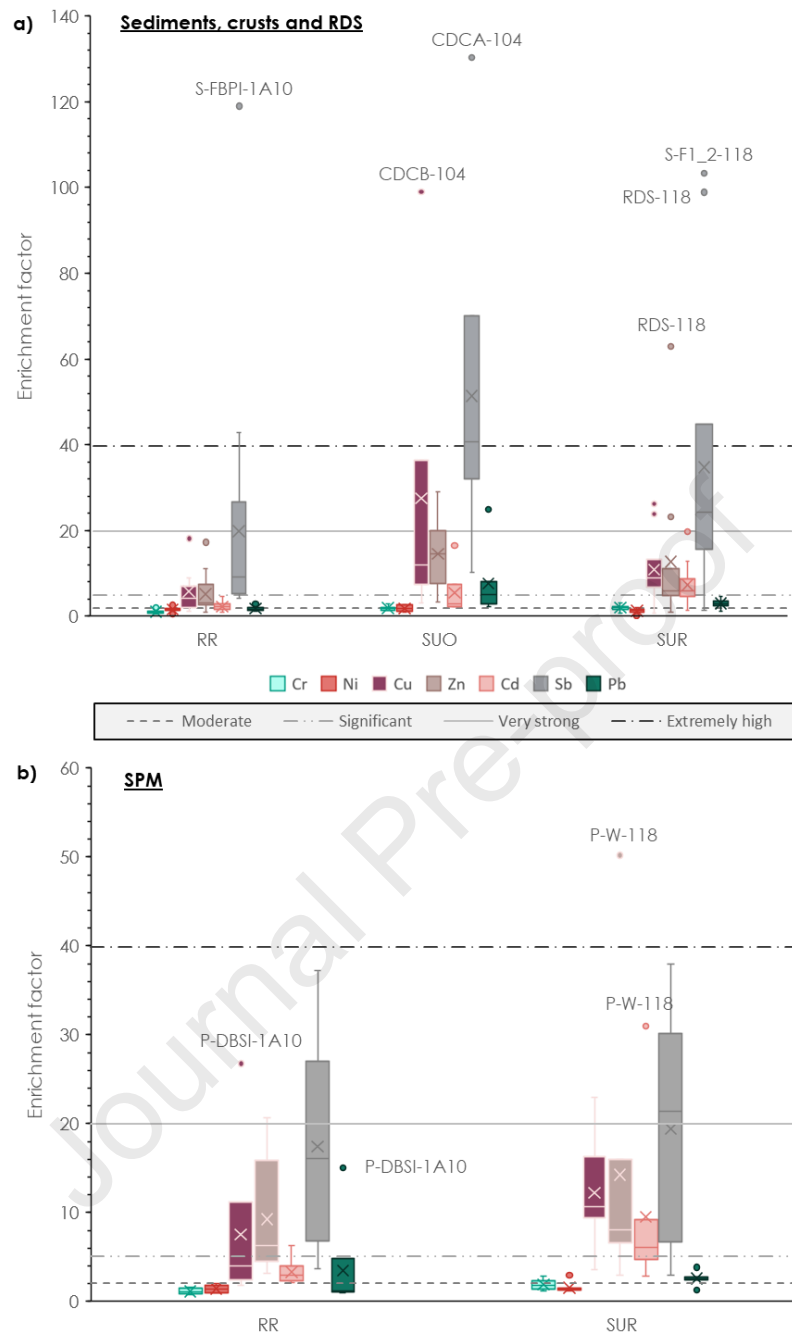
Dissolved Sb concentrations (Table SI-1.5) in SUR pond system range from 0.26  $\mu\text{g.L}^{-1}$  (W-P-118) to 12.5  $\mu\text{g.L}^{-1}$  (W-W-118) in the SUR system and from 0.27  $\mu\text{g.L}^{-1}$  (W-DBFP-2A10) to 13.2  $\mu\text{g.L}^{-1}$  (W-DBSI-1A10) in the RR pond system. The only water sample available in the SUO system shows a concentration of 0.90  $\mu\text{g.L}^{-1}$  (W-DBFP-2A10).

Concentrations of trace elements in sediments, RDS and crusts samples range between 9.8 - 103  $\text{mg.kg}^{-1}$ , <3.5 - 48  $\text{mg.kg}^{-1}$ , 8.5-895  $\text{mg.kg}^{-1}$ , 40 - 2539  $\text{mg.kg}^{-1}$ , 0.2 - 3.2  $\text{mg.kg}^{-1}$ , 0.5 - 93  $\text{mg.kg}^{-1}$  and 8.2 - 444  $\text{mg.kg}^{-1}$  for Cr, Ni, Cu, Zn, Cd, Sb and Pb respectively (Table SI-1.3). The corresponding EFs calculated in sediments, RDS and crusts samples are shown in Figure 2a. In the RR system, Co, Cr, Ni, Cd and Pb are not specifically enriched ( $\text{EF} \leq 5$ ). However, EF of Cu and Zn indicate a significant contamination level ( $1 \leq \text{EF} \leq 19$ ). In the SUO system, mean enrichment contamination level of Co, Cr and Ni are not significant ( $\text{EF} \leq 3$ ). Zinc, Cd and Pb enrichment contamination level is classified as "significantly enriched" ( $2 \leq \text{EF} \leq 29$ ) and Cu enrichment contamination level is very strongly enriched (EF up to 99). In SUR system, Cu enrichment contamination level reach very strong values (up to 26) and extreme values are occasionally observed for Zn (EF = 63 in RDS-118). In the three studied stormwater pond systems, Sb is extremely enriched with respect to the local geochemical background, with maxima EF values as high as 119 in RR (S-FBPI-1A10), 130 in SUO (CDCA-104) and 103 (S-F1\_2-118) in SUR system, attesting of important inputs of Sb in this urban area. It is noteworthy that the Sb natural abundance is low, with a local geochemical background of 0.2 - 0.5  $\text{mg.kg}^{-1}$  (Froger et al., 2018). Therefore, the Sb geochemical anomaly induced by anthropogenic Sb emissions in this urban context is particularly prominent (as reflected by extreme EF values), this trend has already been observed in other large cities (Chen et al., 2008; Gonzales et al., 2016; Dong et al., 2017; Nory et al., 2021).

In comparison with sediments, SPM is a dynamic component in this type of system. Metal concentrations (Table SI-1.4) and EFs (Figure 2b) in SPM have been quantified to give



435 a picture of contamination transfer by surface particles. Concentrations of trace elements in  
436 SPM samples range between 44 - 186 mg.kg<sup>-1</sup>, 18 - 57 mg.kg<sup>-1</sup>, 51 - 985 mg.kg<sup>-1</sup>, 168 - 5019  
437 mg.kg<sup>-1</sup>, 0.6 - 10 mg.kg<sup>-1</sup>, 2 - 83 mg.kg<sup>-1</sup> and 24 - 738 mg.kg<sup>-1</sup> for Cr, Ni, Cu, Zn, Cd, Sb and Pb  
438 respectively. As observed for sediments, Co, Cr and Ni are not particularly enriched in RR and  
439 SUR systems (Figure 2b). In contrast, Cu, Zn and Sb are significantly enriched in RR and SUR  
440 systems. Cadmium is also significantly enriched in SUR system while only moderately  
441 enriched in RR system sediments. Lead is moderately enriched in RR and SUR systems  
442 sediments. Again, Sb presents the highest mean EF in SPM in both RR and SUR systems  
443 sediments. Otherwise, two punctual very strong EF values are observed in the RR system for  
444 the sample P-DBSI-1A10 at 27 for Cu and 21 for Zn. In the SUR system, extreme values are  
445 determined for the sample P-W-118 at 50 for Zn and 31 for Cd. EF determined in SPM of the  
446 RR and SUR systems are comparable between both ponds while their EF are different in  
447 sediments.



448

449 **Figure 2.** Aluminium-normalized enrichment factors for a) sediments, soil, RDS and crusts and  
 450 b) SPM samples compared to the local geochemical background (Thévenot et al., 2007; Froger  
 451 et al., 2018). Chromium EF are shown in cyan, Ni in red, Cu in purple, Zn in taupe, Cd in pink,  
 452 Sb in grey and Pb in green. Eighteen samples are considered for constructing the box plot in  
 453 the RR system, 7 for SUO system, 10 for SUR system. Six samples are considered for SPM  
 454 in RR system and 7 in SUR system. The bottom branch of each boxes represents the minimum  
 455 value, the bottom of the box represents the first quartile, the horizontal line inside the box  
 456 represents the median value, the cross represents the mean value, the top of the box  
 457 represents the third quartile, the dots represent extreme values and the top of the branch  
 458 represents the maximum value for series without extreme values. Horizontal lines indicate the  
 459 level of enrichment according to the classification of Sutherland, (2000).

460

461 The Cu/Sb ratio is frequently used in literature to trace the brake pad contamination in  
462 areas impacted by road traffic (e.g. Stechmann and Dannecker, 1990). Indeed, these two  
463 elements are important constituents of brake pads (Dong et al., 2017). In our study, the local  
464 geochemical background can be estimated at Cu/Sb = 25 (Sb concentration from Froger et al.  
465 (2018) and Cu from Thévenot et al. (2017)). In the SUR system, Cu/Sb reach up to 39 in S-W-  
466 118 (natural pond) and down to 6 in RDS-118, with an average of 12 and 9 if the two samples  
467 from natural pond are excluded (S-W-118 and S-P-118). SUO system Cu/Sb values are  
468 between 6 (RDSB-104) and 35 (CDCB-104) with an average of 12. In RR system the Cu/Sb  
469 values are situated between 4 (S-FBPI-1A10) and 21 (CD2-1A10) with an average of 9.

### 470 3.3. Analysis of Sb sources using $\delta^{123}\text{Sb}$ isotopic signatures

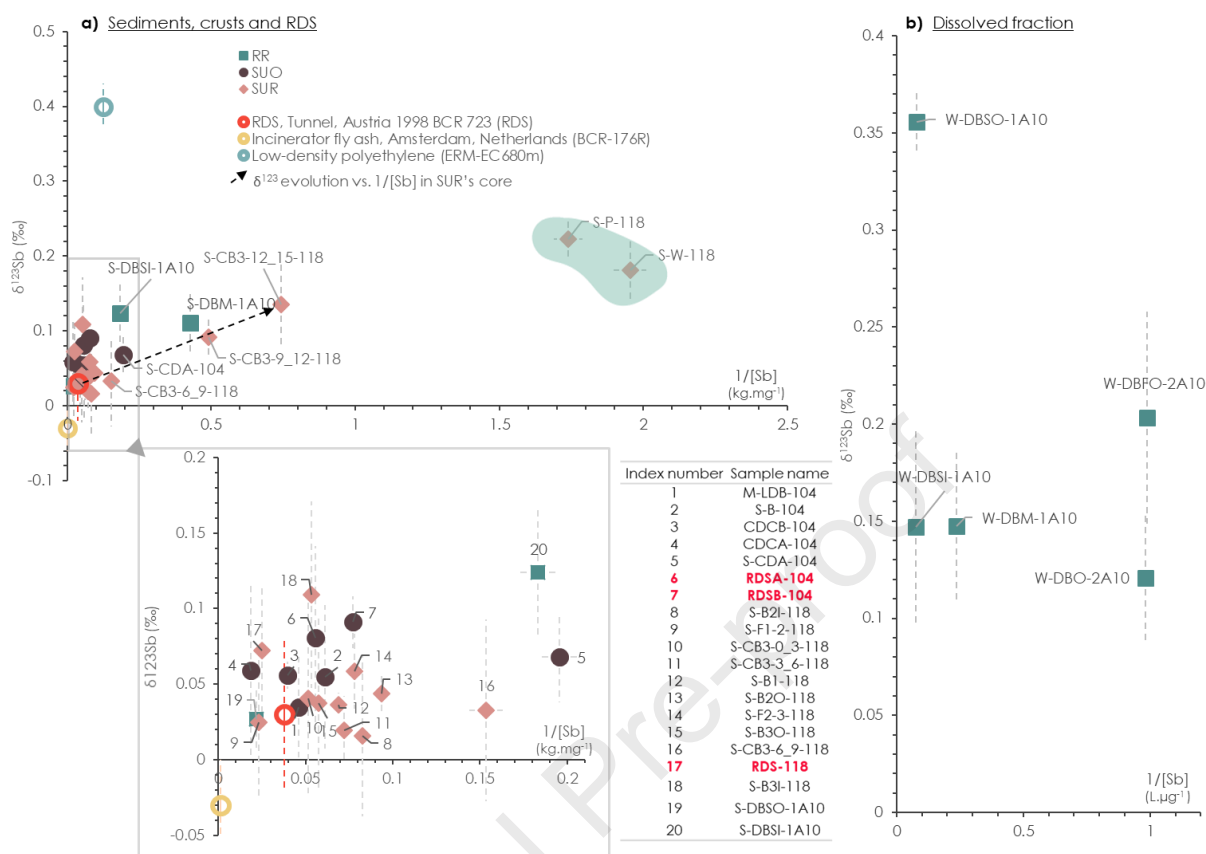
471 Antimony isotopes are applied for the first time to road- affected surface environmental  
472 samples in an attempt to trace the contributions of distinct Sb sources, which could help in  
473 determining the transfer pathways of Sb contamination. Figure 3a and 3b present  $\delta^{123}\text{Sb}$   
474 values as a function of  $1/[\text{Sb}]$  for solid and liquid samples, respectively. Antimony isotopic  
475 compositions of solid samples measured at the three sampling sites range from  $0.02 \pm 0.02\text{‰}$   
476 to  $0.22 \pm 0.03\text{‰}$  with an average of  $0.07 \pm 0.05\text{‰}$  ( $n=25$ ). No significant variation of the average  
477  $\delta^{123}\text{Sb}$  values was observed between the sampling sites ( $\delta^{123}\text{Sb}_{\text{SUO}} = 0.06 \pm 0.02\text{‰}$  ( $n=7$ );  
478  $\delta^{123}\text{Sb}_{\text{SUR}} = 0.06 \pm 0.04\text{‰}$  ( $n=13$ ), excluding the two samples of the natural pond);  $\delta^{123}\text{Sb}_{\text{RR}} =$   
479  $0.09 \pm 0.05\text{‰}$  ( $n=3$ )). On average, values observed for the sediments are closer from those  
480 reported by Ferrari et al. (2021) for the certified reference material of Austrian RDS (BCR 723,  
481  $\delta^{123}\text{Sb} = 0.03 \pm 0.05\text{‰}$ ) than from both Netherlands incinerator fly ash (BCR 176R,  $\delta^{123}\text{Sb} =$   
482  $0.03 \pm 0.03\text{‰}$ ) and low-density polyethylene (ERM-EC 680m,  $\delta^{123}\text{Sb} = 0.40 \pm 0.03\text{‰}$ ). Taken  
483 individually, road deposit sediment (RDS) samples from the SUO and SUR pond systems,  
484 represented in red on the zoom part of Figure 3a, present  $\delta^{123}\text{Sb}$  values and  $1/[\text{Sb}]$  values  
485 relatively close from those of the BCR 723 (Austrian RDS collected in an urban tunnel), with

486  $\delta^{123}\text{Sb} = 0.07 \pm 0.04\text{‰}$  for RDS-118,  $0.08 \pm 0.06\text{‰}$  for RDSA-104 and  $0.09 \pm 0.02\text{‰}$  for RDSB-  
487 104.

488 Two samples of the SUR system highlighted in green in Figure 3a present the highest  
489  $\delta^{123}\text{Sb}$  values ( $0.18 \pm 0.04\text{‰}$  for S-W-118 and  $\delta^{123}\text{Sb} = 0.22 \pm 0.03\text{‰}$  for S-P-118), associated  
490 with low Sb concentrations close to the geochemical background ( $0.51 \text{ mg.kg}^{-1}$  and  $0.57$   
491  $\text{mg.kg}^{-1}$ ). These samples are interpreted as not directly impacted by road emission, which is  
492 consistent with lead isotope ratio data (see SI-3). In SUR system, five sediment samples taken  
493 in a 15 cm core sampled every 3 cm in the B3 SUR basin (Fig. 1) show a decreasing  
494 concentration in Sb as a function of depth in the core ( $19.4 \text{ mg.kg}^{-1}$  for S-CB3-0\_3-118 and  
495  $1.35 \text{ mg.kg}^{-1}$  for S-CB3-12\_15-118) with a concomitant slight increase of  $\delta^{123}\text{Sb}$  values from  
496  $0.02 \pm 0.02\text{‰}$  to  $0.04 \pm 0.06\text{‰}$  for 0 - 9 cm depth and from  $0.09 \pm 0.02\text{‰}$  to  $0.13 \pm 0.06\text{‰}$  for  
497 9 - 15 cm depth.

498 For water samples from the RR system,  $\delta^{123}\text{Sb}$  ranges from  $0.12 \pm 0.03\text{‰}$  to  $0.36 \pm$   
499  $0.02\text{‰}$  with an average of  $0.19 \pm 0.09\text{‰}$  ( $n=5$ ). Thus, dissolved Sb presents an enrichment in  
500 heavy Sb isotope compared to particulate Sb (average  $\delta^{123}\text{Sb}_{\text{RR}} = 0.09 \pm 0.05\text{‰}$ ,  $n=3$ ) at this  
501 RR pond site. Interestingly, at the DBSO sampling point, corresponding to a spillway  
502 separating the settling and filtration ponds, a strong difference between the  $\delta^{123}\text{Sb}$  signatures  
503 of the sediments and the dissolved phase is observed:  $0.03 \pm 0.02\text{‰}$  and  $0.36 \pm 0.02\text{‰}$ ,  
504 respectively. This indicate a significant fractionation of Sb isotopes between the dissolved and  
505 solid phases at this particular spot where reducing conditions were observed.

506



507

508 **Figure 3.**  $\delta^{123}\text{Sb}$  as a function of  $1/[\text{Sb}]$  (Sb concentration in mg.kg<sup>-1</sup> or L.μg<sup>-1</sup>) given for (a)  
 509 sediments, crusts, RDS and (b) water samples (dissolved fraction). Samples from SUR system  
 510 are represented as pink diamonds; sediments, soils, crusts and RDS from SUO system  
 511 are represented as dark purple dots; sediments from RR system are represented as blue filled  
 512 squares and waters as blue contoured squares.  $\delta^{123}\text{Sb}$  values from certified reference material  
 513 published by Ferrari et al. 2021 are also represented: tunnel RDS (BCR 723) in red circle,  
 514 incinerator fly ash (BCR -176R) in yellow circle and low-density polyethylene (ERM-EC 680m)  
 515 in blue circle. The supposed local natural signatures are circled by a light blue area and  
 516 samples from a core situating along the black dotted arrow. RDS sample labels are represented  
 517 in red in the zoom figure and in the associated table.  $\delta^{123}\text{Sb}$  data and Sb concentrations are  
 518 available in Table SI-1.9 in Tables SI-1.3 and SI-1.5, respectively.

519

### 520 3.4. Antimony mineralogy and speciation as studied at the particle and 521 molecular scales

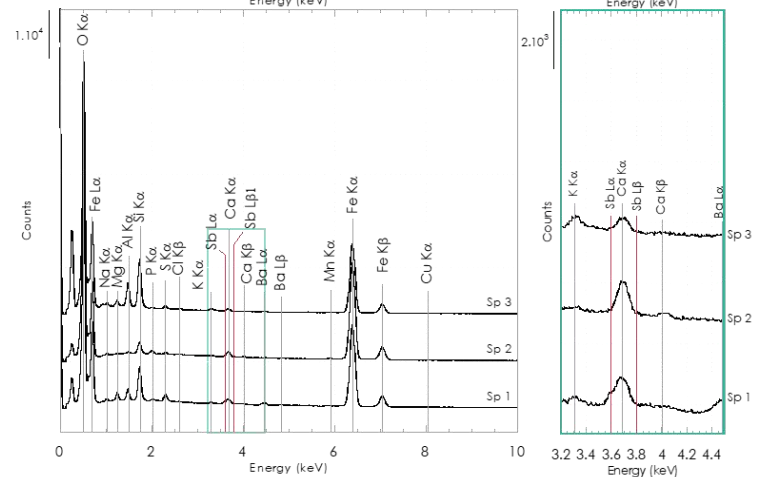
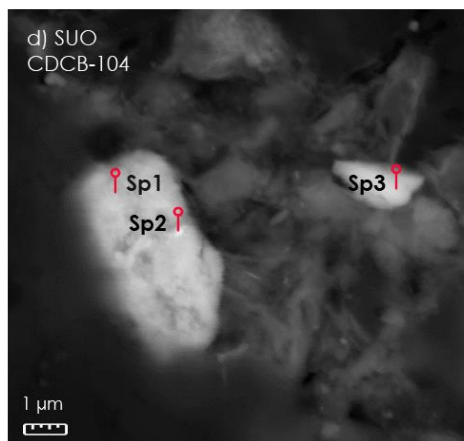
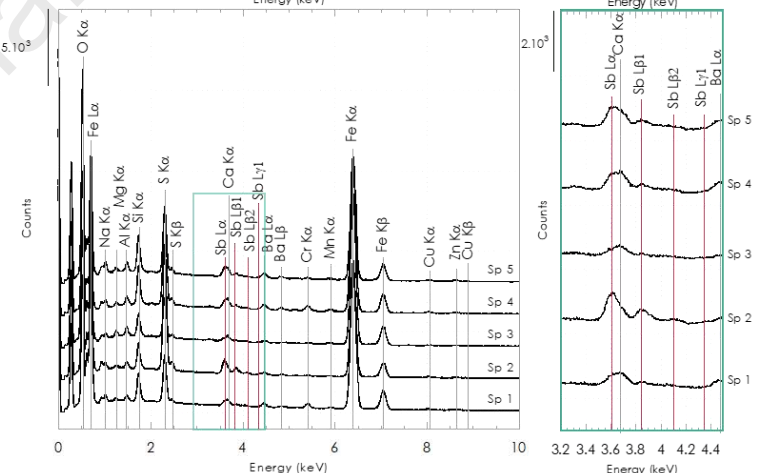
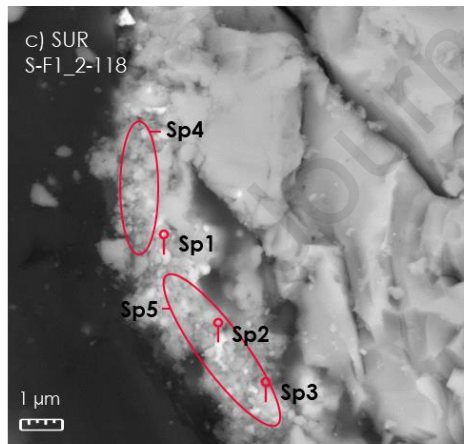
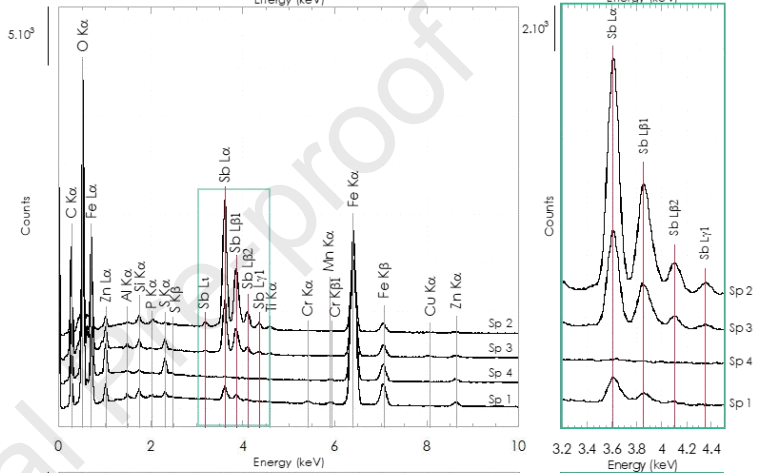
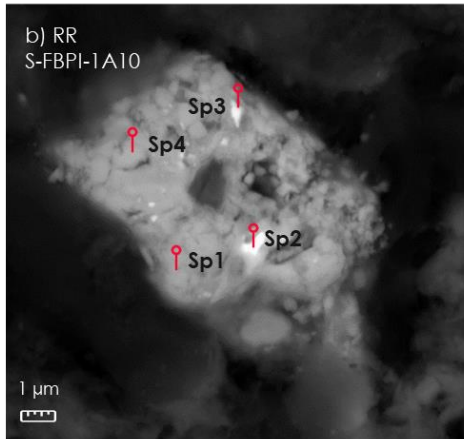
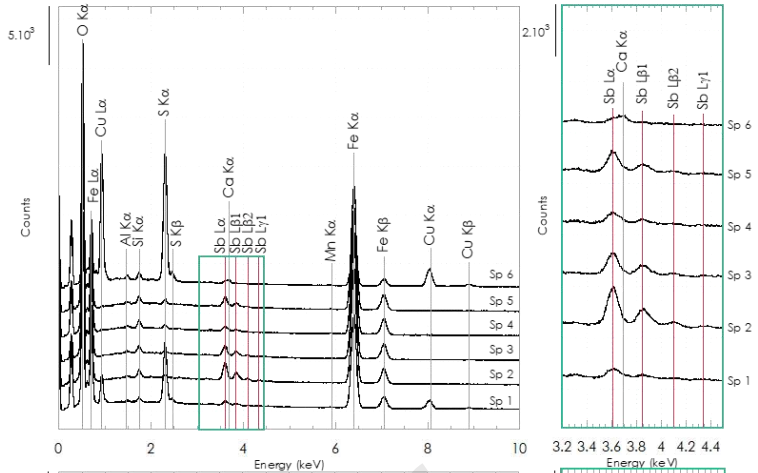
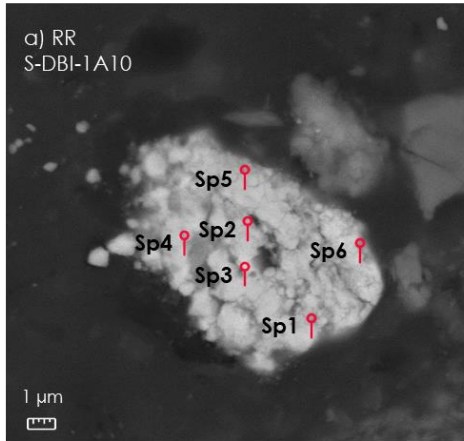
522 To study the mineralogy of solid samples in the stormwater ponds, we have performed  
 523 powder XRD measurements (Fig. SI-1.4). The main mineralogical components (>1%wt) are  
 524 usual geogenic surface minerals such as quartz, calcite and feldspars. At low diffraction angle,

525 the presence of different types of phyllosilicates such as chlorite, illite and kaolinite is observed  
526 on the basis of the (001) reflexions, and small amounts of additional dolomite were observed  
527 in the SUR system samples. For some samples, a weak reflexion around 8.4 Å indicates the  
528 presence of amphibole-type minerals.

529 A systematic SEM-EDXS study was carried out on the samples with the objectives of  
530 (1) documenting the mineralogy of these Sb-enriched samples constituted of both natural and  
531 road derived materials at the aggregate scale, and (2) uncovering discrete Sb-bearing  
532 phase(s) (Fig. 4). Depending on the input of local geogenic particles in the samples, mineral  
533 aggregates of varying sizes ( $>2\ \mu\text{m}$ ) (Fig. SI-1.5) were observed. In particular, in RDS samples,  
534 we observed metallic spherules possibly resulting from abrasion of car/road materials (Fig. SI-  
535 1.7). In general, in all samples, particles made of metallic alloys were observed, e.g. particles  
536 containing Ti, Cr, Cd, Zn and rare earth elements (REE) (Fig. SI-1.6). An important contribution  
537 of iron oxyhydroxides/oxides was also observed. Antimony was detected in particles in the  
538 three pond systems *via* punctual EDXS analysis using the *L*-emission lines as diagnostic  
539 spectral pattern ( $L\alpha_1$  3,604.72 eV,  $L\alpha_2$  3,595.32 eV,  $L\beta_1$  3,843.57 eV,  $L\beta_2$  4,100.78 eV,  $L\gamma_1$   
540 4,347.79 eV and  $L\gamma_2$  3,192 eV). In the RR samples S-DBI-1A10 (Fig. 4a) and S-FBPI-1A10 (Fig.  
541 4b), the analysed Sb-bearing particles showed different chemical compositions depending on  
542 the spot where the analysis was performed. Indeed, the presence of Sb is always concomitant  
543 with the one of Fe, while Sp1 and Sp6 spots (Fig. 4a) qualitatively show the additional presence  
544 of S, Cu and Na. The sample S-FBPI-1A10 (Fig. 4b) shows the presence of Zn and particularly  
545 high level of Sb at discrete submicrometric spots, especially in Sp2 where Sb content is  
546 qualitatively higher than Fe. In the sample S-F1\_2-118 from the SUR system (Fig. 4c), Sb was  
547 also found as submicrometric particles associated with Fe oxyhydroxides/oxides. In S-F1\_2-  
548 118, punctual EDXS spectra (Sp1, Sp2 and Sp3) and EDXS spectra of areas (Sp4 and Sp5)  
549 show roughly the same amount of S, Fe and Cu, but Cr and Ba are also detected. Sp2  
550 spectrum, taken on the spot presenting the higher backscattering intensity accordingly shows  
551 the highest Sb signal compared to spectra Sp1 and Sp3. In SUO system, on sample

552 CDCB-104 (Fig. 4d), the particle containing Sb was also observed as associated with an iron-  
553 containing particle (containing also major elements such as Ca). Because the Ca *K*-emission  
554 line overlaps with the main *L*-emission line of Sb, the signal is more difficult to distinguish but  
555 remains visible, for instance in the Sp1 spectra (Fig. 4d) in which Cu, S and Ba are also  
556 detected.

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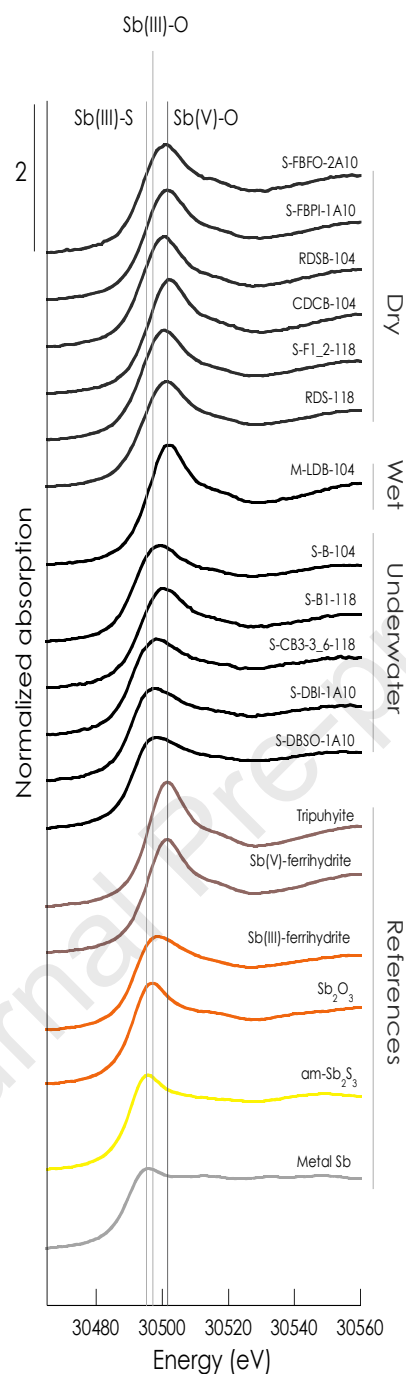


558 **Figure 4.** SEM images taken in backscattering mode (left), and qualitative EDXS analyses on  
559 the right for three samples representative of each highway stormwater pond systems SUR,  
560 SUO and RR. A zoom between 3.2 and 4.4 KeV on the X-Ray emission spectra (green  
561 rectangle) shows the presence of Sb on the basis of the  $L\alpha_1$  to Li emission lines. Sediments  
562 S-DBI-1A10 (a) and dry sediment S-FBPI-1A10 (b) (RR system) are represented on the first  
563 and second lines, dry sediment S-F1\_2-118 (c) (SUR system) on the second line and crust  
564 CDCB-104 (d) (SUO system) on the bottom line.

565

566 Calibrated and normalized XANES data include both samples from the field and  
567 selected reference compounds (Fig. 5). The reference compounds selected in which Sb is  
568 under the Sb(V)-O form are tripuyite ( $FeSbO_4$ ) and ferrihydrite co-precipitated in the presence  
569 of dissolved Sb(V). The reference compounds selected in which Sb is under the Sb(III)-O form  
570 are ferrihydrite co-precipitated in the presence of dissolved Sb(III) and  $Sb_2O_3$ . Finally, the  
571 chosen reference compound representative of the Sb(III)-S molecular environment is  
572 amorphous  $Sb_2S_3$ . Additionally, the metallic Sb foil was considered as a Sb(0) metal/alloy  
573 reference. Qualitative examination of XANES spectra (Fig. 5) shows that the maximum of  
574 absorption of the "dry" samples is shifted towards the higher energies, *i.e.* the oxidized species  
575 with oxygen ligand Sb(V)-O. On the contrary, the "Underwater" samples show maxima shifted  
576 towards lower absorption energies and therefore present a non-negligible contribution of  
577 reduced Sb species (*e.g.* Sb(III)-O and/or Sb(III)-S).

578

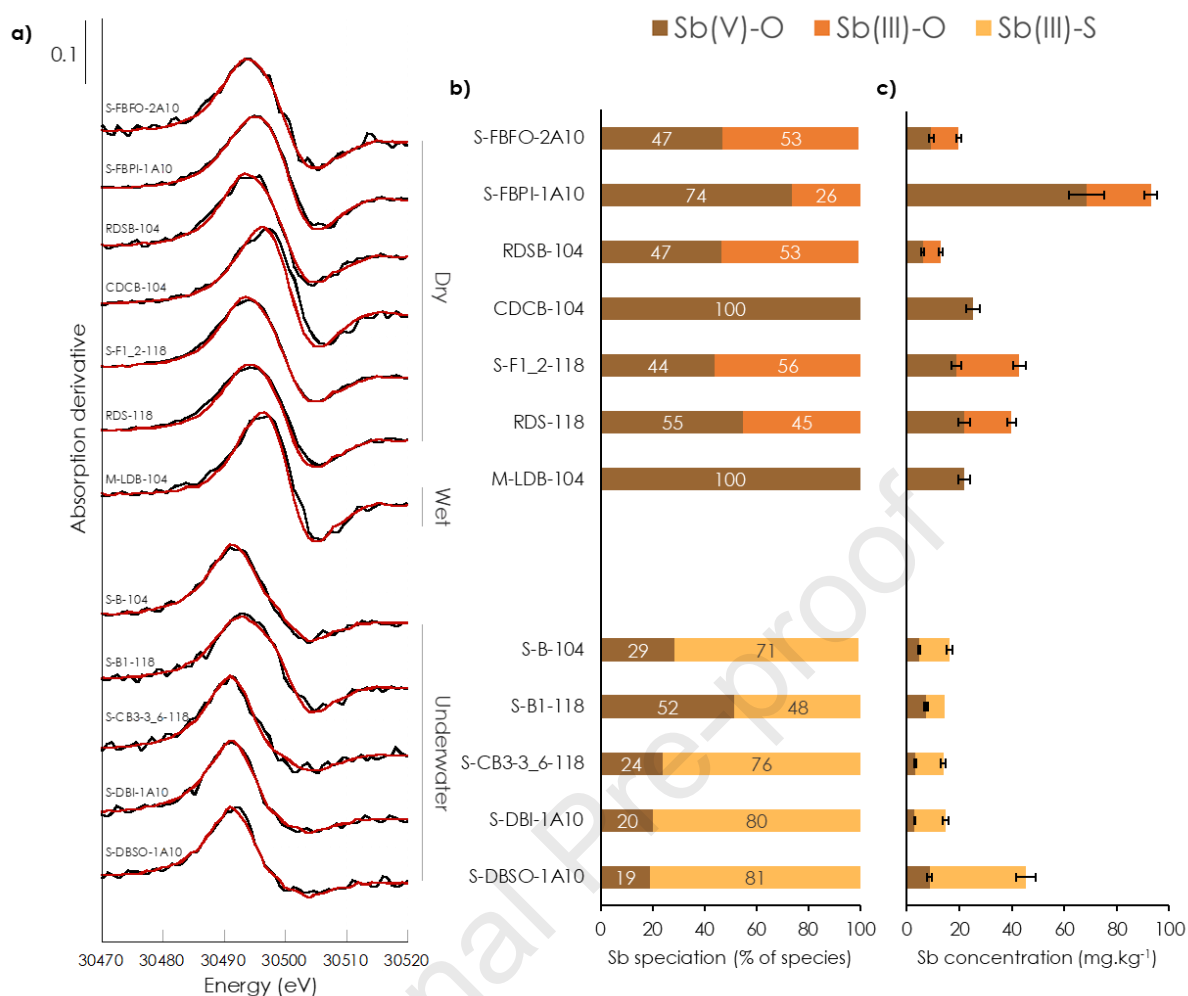


579

580 **Figure 5.** Antimony *K*-edge XANES spectra of dry and wet samples, underwater samples  
 581 (black) collected in the three studied sites in the Paris region (France), Sb(V)-O references  
 582 (brown) are tripuhyite ( $\text{FeSbO}_4$ ) and Sb(V) co-precipitated ferrihydrite; Sb(III) references are  
 583 Sb(III) co-precipitated ferrihydrite,  $\text{Sb}_2\text{O}_3$  (orange) and amorphous  $\text{Sb}_2\text{S}_3$  (yellow); Sb(0) is  
 584 represented by metal Sb (grey). Vertical lines represent the maximum of XANES signal for  
 585 known chemical environments and ligands, namely Sb(V)-O (30 501 eV), Sb(III)-O (30,497-  
 586 30,499 eV), Sb(III)-S (30,496 eV), and Sb(0) (=Sb-Sb, 30,496 eV).

587

588 To quantify the contribution of different oxidation states and ligands in Sb speciation,  
589 we proceeded to a LCF analysis on the derivative of the Sb *K*-edge XANES spectra using  
590 three reference samples representative of the system geochemistry, namely Sb(V)-ferrihydrite  
591 (Sb(V)-O), Sb(III)-ferrihydrite (Sb(III)-O), and amorphous Sb<sub>2</sub>S<sub>3</sub> (Sb(III)-S). Results of LCF are  
592 presented on Figure 6 and in Table SI-1.10. In the “dry” samples, the Sb(V)-O form dominates  
593 although the Sb(III)-O species are present in significant proportions, between 26% and 56%,  
594 except in CDCB-104 in which only the Sb(V)-O form is detected. Likewise, the “wet” sample  
595 M-LDB-104 contains only Sb(V)-O species. In contrast, in the “underwater” samples, Sb  
596 speciation is dominated by the Sb(III)-S species (from 48% to 81%). Figure 6c presents Sb  
597 speciation normalized to total Sb concentrations in the samples. Thus, we observe that  
598 “underwater” samples presenting the main Sb(III)-S signature are likely less concentrated in  
599 Sb, between 13.9 mg.kg<sup>-1</sup> for S-CB3-3\_6-118 to 45.3 mg.kg<sup>-1</sup> for S-DBSO-1A10 than “dry”  
600 samples presenting concentrations up to 93 mg.kg<sup>-1</sup> in the S-FBPI-1A10 sample (Fig. 6c).



601

602 **Figure 6.** (a) Results of the linear combination fitting procedure applied on the absorption first  
 603 derivative of XANES spectra (experimental data in black and fit in red). (b) Proportion of  
 604 Sb(V)-O species (brown), Sb(III)-O species (orange) and Sb(III)-S species (yellow) normalized  
 605 to 100% (more details of the species in supplementary information). (c) Results of LCF  
 606 normalized (%) to total Sb concentration (mg.kg<sup>-1</sup>) in the samples. Errors on components  
 607 determined by LCF are considered to be 10%.

608

## 609 4. Discussion

### 610 4.1. Geochemical parameters as tracers of emission sources in near-road 611 environments

612 Radiogenic Pb isotope ratios validate the 2 categories established by the land-use  
 613 observed in the drained area of the systems: semi-urban (SUO and SUR) and rural systems  
 614 (RR), on the basis of our knowledge of Pb isotopic endmembers in urban areas. Moreover,  
 615 heterogeneous isotopic signatures observed and the close to former lead gasoline signatures

616 in 2 samples of the RR system show that Pb isotopes cannot be directly used to infer the age  
617 of highway stormwater ponds (see SI-2). Indeed, former lead gasoline signature has been  
618 shown to still contributed to impact urban environments (Ayrault et al., 2012; Resongles et al.,  
619 2021).

620 Enrichment factors ranging between 0.4 and 130 are observed for Co, Cr, Ni, Cu, Zn, Cd, Sb  
621 and Pb. They are of the same magnitude with those previously observed in near road  
622 environments (Meland et al., 2010). Different sources for these metals are evoked in the  
623 literature, among which abrasion of brake linings for Cu, Sb, Zn, Pb, Cr and, to a lesser extent,  
624 of Ni and Cd (Sörme and Lagerkvist, 2002; Hjortenkrans et al., 2007; Thorpe and Harrison,  
625 2008). Zinc, which is strongly enriched in our system, is also used in tires and motorway crash  
626 barriers (Sörme and Lagerkvist, 2002; Zhang et al., 2004; Hjortenkrans et al., 2007). Cobalt,  
627 Zn, Pb, Cr, Ni and Cd, as constituents of car bodies, can be released to the environment by  
628 simple rain leaching (Störm and Lagerkvist, 2002), probably explaining a part of the emissions  
629 given the high flux of vehicles on the road investigated (Table 1). In this study, enrichments in  
630 Cd, Cr and Ni are found to be more limited in sediments and SPM in comparison with the data  
631 of Hjortenkrans et al. (2007) in road environments. Here, the higher enrichment factors of Pb  
632 in semi-urban systems sediments compared to the rural system is in line with the results of Pb  
633 isotopic signatures that indicate a major urban source contribution. Cadmium and Cr,  
634 presenting higher concentrations in the SUR system compared to RR and SUO systems, (Fig.  
635 SI-1.2) might have a different or an additional source at SUR compared to RR and SUO (Fig.  
636 2). Both Cr and Cd enrichments occurred in the third basin (B3, SUR system), also connected  
637 to the natural pond (Fig. 1), itself hydrologically connected to the overlying Fontainebleau sand  
638 aquifer. We thus hypothesize that Cd and Cr could have been emitted by past industrial/urban  
639 activities (Avino et al., 2008; Byrne et al., 2017) on the Plateau of Saclay situated upstream or  
640 by a geogenic source from the Fontainebleau sands aquifer (which geochemistry is not yet  
641 documented). Correlations of Sb with Cu concentrations in the solid phase (Fig. SI-1.2) point  
642 to a potential common source such as emission from brake pads (Thorpe and Harrison, 2008).

643 If the ratio Cu/Sb is constant in the road environment, and different from that of the  
644 geochemical background, it is then possible to determine the anthropogenic contribution in the  
645 environment studied. Figure SI-1.8 represents Cu/Sb ratios of the collected solid samples as  
646 compared to the Cu/Sb ratios listed in the literature. In the literature, brake pads Cu/Sb is 16.5  
647 on average with variations from 3.5 to 29 (Weckwerth, 2001; Hjortenkrans et al., 2007; Dong  
648 et al., 2017). In Sweden, this high range of observed values was explained by the occurrence  
649 of different brake suppliers. In the study of Hjortenkrans et al. (2006) focusing on PM<sub>10</sub>, Cu/Sb  
650 are between 4.9 and 15.1 with a median of 5.5. Top soils collected at less than 0.5 m from the  
651 road pavement show mean Cu/Sb of 20 (Hjortenkrans et al., 2006) and Cu/Sb ratio of 28 was  
652 measured in RDS (Dong et al., 2017). Here, the RDS samples show low Cu/Sb values, ( $6 \leq$   
653  $\text{Cu/Sb} \leq 7$ ). Excluding the SUR natural pond ( $\text{Cu/Sb} \geq 14.8$ ), the underwater sediments show  
654 Cu/Sb values between 5.2 and 10.7, which is well below the values determined for the local  
655 geochemical background ( $\text{Cu/Sb} = 25$ ). A possible source of variation could be that Sb and Cu  
656 could also be emitted by oil leakages containing anti-frictions materials such as tin-based  
657 babbitt alloys used as dry lubricants in engine bearings in case of oil pump failure, themselves  
658 presenting various compositions (Paleu et al., 2016).

659 Zinc concentrations in solid samples are positively correlated with Sb concentrations (Fig. SI-  
660 1.2,  $R^2$  of 0.92 and 0.73 for RR and SUO respectively, and 0.65 for SUR (0.99 excluding RDS-  
661 118)), also pointing to a possible common source in road environments. In the SUR system,  
662 the RDS sample (RDS-118) might contain a fraction of galvanized steel issued from the  
663 sampled surface, explaining its high Zn concentration. As the Zn-Sb correlation is observed  
664 both in urban and rural environments, the source of emission is likely due to abrasion of  
665 vehicles constituents, including brake pads (Hjortenkrans et al., 2007).

666

#### 667 **4.2. Antimony elemental and isotopic geochemistry and associated sources**

668 Antimony concentrations in dissolved fractions (0.26 to 13.2  $\mu\text{g.L}^{-1}$ ) are comparable to  
669 the concentrations measured in a stormwater pond in Oxford (0.67 - 8.19  $\mu\text{g.L}^{-1}$ ,

670 Kamalakkannan et al., 2004). These values are higher than the ones observed in the Orge  
671 River even in the highly urbanized areas ( $0.23\text{-}0.44\ \mu\text{g.L}^{-1}$  at Viry-Châtillon, Le Pape et al.,  
672 2012). In the SUR natural pond not impacted by traffic runoff, the high dissolved concentration  
673 of Sb ( $12.5\ \mu\text{g.L}^{-1}$ ) does not reflect the concentrations in the corresponding sediment ( $0.5$   
674  $\text{mg.kg}^{-1}$ ) and SPM ( $6.1\ \text{mg.kg}^{-1}$ ) fractions. Explaining this particular enrichment in dissolved Sb  
675 would need further research to determine if it was a punctual anomaly (e.g. local contamination  
676 of the overlying aquifer) or a permanent input from the Fontainebleau sand aquifer waters. Our  
677 values only exceptionally exceed the European guidelines for Sb concentration in drinking  
678 water fixed at  $10\ \mu\text{g.L}^{-1}$  (directive UE 2020/2184) and are below the drinking water guidelines  
679 for antimony ( $<20\ \mu\text{g.L}^{-1}$ ) as stated by the World Health Organization (Guidelines for Drinking  
680 water quality, 2017).

681 All the solid samples collected in the ponds, including sediments, crusts and soils, present an  
682 average  $\delta^{123}\text{Sb}$  signature of  $0.07 \pm 0.05\text{‰}$  ( $n=25$ ), which is close to the RDS reference material  
683 (BCR-723,  $\delta^{123}\text{Sb}$  of  $0.03\text{‰}$ , Ferrari et al., 2021). Additionally, the  $\delta^{123}\text{Sb}$  signatures of RDS  
684 samples measured in this study (Fig. 3) are also close to the BCR-723 signature. The RDS  
685 signature could then reflect a mean isotopic signature of Sb in brake pads in use in France  
686 over the last decennials. The low concentrated sediment samples in the SUR natural pond ( $0.5$   
687  $\text{-}0.6\ \text{mg.kg}^{-1}$ ) show heavier  $\delta^{123}\text{Sb}$  signatures (S-W-118  $18 \pm 0.04\text{‰}$  and S-P-118  $22 \pm 0.03\text{‰}$ )  
688 than most of the samples from the stormwater ponds on the same site (Fig. 3). We could thus  
689 hypothesize that these samples could trace the local geochemical endmember (Fig. 3, in  
690 green), or a different source resulting from the industrial activities of the Saclay plateau located  
691 above. Nevertheless, the hypothesis of a local Sb contamination source different from the road  
692 is less plausible considering the low concentrations and EF measured in the natural pond.  
693 Moreover,  $\delta^{123}\text{Sb}$  and the Sb concentration of the core samples vary slightly from the bottom  
694 to the top with a heavier signature  $\delta^{123}\text{Sb}$   $0.13\text{‰}$  at the bottom ( $1.3\ \text{mg.kg}^{-1}$ ) going down to  
695  $0.04\text{‰}$  at the top sample with a higher concentration ( $19\ \text{mg.kg}^{-1}$ ). Considering the local  
696 background signature determined as  $0.18\text{‰} - 0.22\text{‰}$ , this variation could be explained by the

697 higher contribution of geogenic materials in deeper samples. Albeit global  $\delta^{123}\text{Sb}$  signature  
698 points towards a close range of values, the local variation observed on some samples could  
699 putatively be ascribed to fractionation due to post-depositional processes. Indeed, in the RR-  
700 2A10 pond, two samples present diverging  $\delta^{123}\text{Sb}$  values in the dissolved fraction (W-DBFO-  
701 2A10 and W-DBO-2A10) while having the same Sb concentration. DBFO could represent the  
702  $\delta^{123}\text{Sb}$  value for input water whereas DBO could represent the equilibrated value after a longer  
703 residence time in the pond. This might be due to isotope fractionation between the dissolved  
704 and solid fractions in the pond due to specific biogeochemical processes  
705 (reduction/oxidation/ligand exchange) occurring within the sediments, potentially attesting of  
706 Sb exchanges between the solid phase and the overlying water column. In the RR-1A10 reed-  
707 planted pond, particularly interesting observations are made for the samples DBSI, DBM, and  
708 DBSO, located from the entrance to the exit of the settling pond, respectively. For DBSI and  
709 DBM, dissolved and sediment fractions present similar  $\delta^{123}\text{Sb}$  signatures (DBSI,  $0.15 \pm 0.05\text{‰}$   
710 dissolved vs.  $0.12 \pm 0.04\text{‰}$  solid, and DBM,  $0.15 \pm 0.04\text{‰}$  dissolved vs.  $0.11 \pm 0.04\text{‰}$  solid)  
711 whereas for DBSO they significantly differ ( $0.36 \pm 0.02\text{‰}$  dissolved vs.  $0.03 \pm 0.02\text{‰}$  solid).  
712 We could hypothesize that this particular fractionation at the DBSO site could possibly be a  
713 consequence of Sb(V) reduction to Sb(III) under anoxic conditions, and/or to ligand exchange  
714 from oxygen to sulphur (Rouxel et al., 2003; Ferrari et al., 2022), which would be supported by  
715 the LCF-XANES analysis on this Sb-rich ( $45.3 \pm 2.7 \text{ mg.kg}^{-1}$ ) sample showing an important  
716 contribution of reduced Sb (Sb(III)-S =  $81 \pm 10\%$  vs. Sb(V)-O =  $19 \pm 10\%$ ). A smell of sulphide  
717 was also noticed at the DBSO sampling point, indicative of sulphide-producing conditions that  
718 might also induce a fractionation of Sb between dissolved and solid fractions, for instance due  
719 to production of thio-Sb intermediates (Ye et al., 2019). Alternatively, other physico-chemical  
720 processes could play a role in Sb isotope fractionation. For instance, preferential adsorption of  
721 light Sb isotope has been observed with Sb(V) on alumina due to kinetic effects, leaving  
722 heavier Sb isotope in aqueous phase (Zhou et al., 2022).



723 SEM-EDXS allowed us to observe discrete phases carrying Sb (Fig. 4) directly pointing to the  
724 brake pad source. In the three systems Sb was similarly observed on micro-particles with high  
725 backscattering signal associated to iron oxides (Fig. 4). In these particles, Fe, S, Cu, Zn and  
726 Ba are observed in addition to Sb (Fig. 4), as it has already been observed in some brake pads  
727 (Ingo et al., 2004). Due to brake friction, the high temperature leads to the oxidation of  $\text{Sb}_2\text{S}_3$   
728 lubricant and oxidizes  $\text{Sb}_2\text{S}_3$  into  $\text{Sb}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_3$  and/or  $\text{Sb}_2\text{O}_4$ , depending on the temperature  
729 generated by the braking process and the initial composition of brake pads (Ingo et al., 2004;  
730 Cho et al., 2006; Martinez and Echeberria, 2016). These Sb oxides would then react with  
731 metallic iron included in the brake pad to form iron oxides, metallic Sb, and/or Fe-Sb containing  
732 alloys (Matějka et al., 2011; Martinez and Echeberria, 2016). Even if its use will probably tend  
733 to decrease since health and environment safety decisions in the USA are leading to a ban of  
734 Sb in brake pads (US EPA Copper-Free Brake Initiative), these observations and the nature  
735 of phases containing Sb observed by SEM-EDXS strongly suggest that brake pads are a  
736 present-day source of Sb emission from road traffic at the sampling sites. It is important to note  
737 that Sb could also be present, even in a large extent, as associated with mineral phases at  
738 lower concentration, non-detectable with the SEM-EDXS method. To obtain an image of Sb  
739 speciation at the scale of the bulk sample, taking also into account the Sb dispersed within  
740 other mineralogical phases at trace level, we applied X-ray absorption spectroscopy at the Sb  
741 *K*-edge.

### 742 **4.3. Antimony geochemical reactivity in road impacted surface**

#### 743 **environments**

744 Linear combination fits of XANES derivative spectra at the Sb *K*-edge show that both  
745 Sb(V)-O and Sb(III)-O are observed in solids sampled in “dry” oxic conditions (Fig. 5). In a  
746 previous study, Sb(III) and Sb(V) with both oxygen and sulphur ligands have been detected in  
747 urban road samples such as RDS and aerosols (10  $\mu\text{m}$  and 2.5  $\mu\text{m}$ ) (Varrica et al., 2013). In  
748 this latter study, the authors interpret their speciation as a result of  $\text{Sb}_2\text{S}_3$ -containing brake pad  
749 abrasion producing Sb oxides ( $\text{Sb}_2\text{O}_3$  (Sb(III)-O), and  $\text{Sb}_2\text{O}_5$  (Sb(V)-O) species) as also

750 identified by Matějka et al. (2011). Here, we confirm that, in dust directly produced by road  
751 traffic, *i.e.* in the RDS sampled upstream from the studied pond systems, mixed  
752 Sb(V)-O/Sb(III)-O oxidation states were present, which would also be in agreement with  
753 emissions from brake pads. This tends to indicate, together with SEM-EDXS observations  
754 previously discussed, that this source is still active, from direct brake pad abrasion, or from  
755 leaching of ancient asphalt surfaces (Dong et al., 2017; Spreadbury et al., 2021).

756 Antimony speciation is driven by both biotic and abiotic geochemical processes including direct  
757 Sb bacterial respiration (Li et al., 2016; Loni et al., 2019) and secondary Sb reduction by  
758 reductants produced by bacterial respiration. For instance, antimony(V) reduction can be  
759 caused by local production of electron donors such as Fe(II) or sulphides, themselves  
760 biogenically produced in anoxic/suboxic conditions by Fe(III)-reducing or sulphide producing  
761 bacteria. Fe(III)-oxy(hydro)xides bioreduction induces a release of Fe(II) into the water and a  
762 precipitation of secondary Fe(III) bearing minerals (Burton et al., 2019, 2020). This precipitation  
763 may cause the incorporation of Sb(V) species in the neoformed minerals *via* Fe(III) substitution  
764 (Hockmann et al., 2021) or Sb(V) reduction to Sb(III) (Kirsch et al., 2008). Sb(V) reduction can  
765 also be mediated by reduced organic matter such as humic acids when associated to Fe(II) in  
766 solution (Karimian et al., 2019). In turn, sulphide produced by bacteria can result in Fe-  
767 oxy(hydro)xides sulphidation followed by the release of Sb(III) and the subsequent formation  
768 of Sb(III)-S species (Ye et al., 2019; Hockmann et al., 2020; Ye and Jing, 2022). Finally, abiotic  
769 processes resulting from surface electrons transfer from Fe and Mn oxyhydroxides to Sb(III)  
770 species under oxic atmosphere has been shown to occur at both acidic and neutral pH,  
771 resulting in Sb(III) oxidation (Belzile et al., 2001).

772 No direct speciation data are currently available on Sb emitted from road dust contamination  
773 when transferred to surrounding surface environments such as soils, sediments and  
774 hydrosystems. In the studied pond systems, representative of surface accumulator media, two  
775 distinct patterns were discernible. Indeed, solids sampled in oxic “dry” conditions present  
776 exclusively oxygen-bound form of Sb, while an additional sulphur-bound form is observed for

777 suboxic underwater samples. This observation would support the hypothesis of local  
778 biogeochemical transformations. This is in line with the results of Arsic et al. (2018) who  
779 observed a significant contribution of Sb(III)-S species (25% to 60%) in their experiments of  
780 anoxic sediment aged under a water column and with Ye and Jing (2022) showing the  
781 immobilisation of Sb in the  $Sb_2S_3$  form due to S(0) reduction by *Shewanella oneidensis* MR-1  
782 in the presence of Sb(III) adsorbed goethite. Here, we observe an important contribution of  
783 Sb(III)-S (48% to 80%) in the underwater samples. Since  $Sb_2S_3$  is constitutive of brake pads,  
784 we cannot exclude that part the measured Sb(III)-S contribution could originate directly from  
785  $Sb_2S_3$  fragments even if its oxidation is mainly expected due to brake friction (Matějka et al.,  
786 2011; Martinez and Echeberria, 2016). If produced by local biogeochemical reactions as  
787 shown in the study of Arsic et al. (2018), in the present study, questions remain on the actual  
788 identity of the Sb(III)-S phases present in our samples. Indeed, such a Sb(III)-S XANES  
789 spectral contribution could be the signature of Sb bonding to thiol functional groups of organic  
790 matter (OM) (Besold et al., 2019a, 2019b) or Sb(III) association with iron sulphide such as FeS  
791 or  $FeS_2$  (Kirch et al., 2008; Hockmann et al., 2020), or of amorphous Sb-sulphide as observed  
792 elsewhere (Kulp et al., 2014; Bennett et al., 2017; Besold et al., 2019; Ye and Jing, 2022).

793 Thioantimonate species have been designated as potential intermediates of these sulphidation  
794 reactions, having particular consequences on Sb mobility for instance by limiting Sb affinity to  
795 iron oxides (Ye et al., 2019, 2021). The presence of minor amounts of such thio-Sb forms,  
796 including within the solid phase, could not be excluded since XANES spectra of sorbed thio-  
797 Sb at the Sb *K*-edge should contribute in between the Sb-O and Sb-S species. In the literature,  
798 the sulphidation process of particles such as Sb(V)-containing oxyhydroxides has recently  
799 been reported to result in an important Sb mobilization towards the aqueous phase, likely  
800 resulting in Sb depletion in the solid fraction (Hockmann et al., 2020). Here, Sb concentrations  
801 were on average lower in underwater samples compared to the ones sampled on surfaces  
802 exposed to air, which would be in line with this process. Alternatively, this difference of

803 concentration could be due to dilution of Sb inputs by detrital particles accumulating in the  
804 basins.

805 In underwater samples of the present study, no statistically significant contribution from  
806 Sb(III)-O species were detected. In contrast, Arsic et al. (2018) have observed this species  
807 even under anoxic conditions, and Besold et al. (2019a) also observed an important Sb(III)-O  
808 contribution in peatland samples. In this latter study, the authors conclude that the high organic  
809 content and/or the particular nature of OM would stabilize the Sb(III)-O form, which could also  
810 be the case for Arsic et al. (2018). In their study concerning Fe oxyhydroxides sulphidation  
811 experiments, Hockmann et al. (2020) observed a weak contribution of the Sb(III)-O species in  
812 the solids, in particular in their low sulphidic system, which could be related to the fact that only  
813 a negligible fraction of antimonite is detected in the aqueous phase.

814 In the underwater sample S-DBSO-1A10, situated upstream in the RR pond system, the major  
815 species are Sb(III)-S ( $84 \pm 10\%$ ) with only  $16 \pm 10\%$  of Sb(V)-O, while in the dry sample  
816 S-FBPI-1A10, located very close on the same hydrologic pathway but at the open air, our  
817 results show 74% of Sb(V)-O and 26% of Sb(III)-O. This means that over a short spatial course,  
818 Sb shows significant differences in its redox geochemistry. Thus, this would confirm that Sb  
819 speciation is particularly versatile in such surface environments, likely driven by the local redox  
820 potential. Indeed, changes from anoxic to oxic media result in dramatic changes of Sb oxidation  
821 state and coordination chemistry. In addition, the fact that dry sample is more concentrated in  
822 Sb than underwater sample would likely support the hypothesis of a Sb transfer, for instance  
823 in the dissolved phase, and potentially resulting from release due to Sb sulphidation upstream  
824 in the pond as evoked previously. These results raise questions about the mobility properties  
825 of Sb at the liquid/solid interface in stormwater ponds, in particular because water fluctuations  
826 often occur in these ponds, due to evaporation associated with long dry periods and storm  
827 events or management operations.

## 828 5. Conclusion

829

830 This study brings new information about antimony isotope geochemistry and speciation in  
831 stormwater pond accumulator media representative of surface environments impacted by road  
832 runoff such as urban areas. Both semi-urban and rural ponds are observed to be contaminated  
833 with a cocktail of inorganic contaminants clearly identified as emitted by road traffic (Cu, Zn,  
834 Sb and Pb). Additional inorganic contaminants (Cd, Ni and Cr) are particularly observed in  
835 urban ponds and their presence is interpreted to originate from anthropogenic urban/industrial  
836 activities. The Pb isotope ratio dataset shows that the impact of urban areas is significant even  
837 if the sampling sites are not directly connected to urban networks, which would reflect a  
838 contamination at a larger scale, likely due to atmospheric particle inputs or to urban particles  
839 reemitted by leaching of vehicles during rain events. Antimony is the most enriched element in  
840 both rural and urban highway stormwater ponds exposed to the road traffic source. For the  
841 first time, Sb isotope composition ( $\delta^{123}\text{Sb}$ ) of road dust sediments is characterized and shows  
842 a homogenous value among the different road-impacted sites, giving access to the mean  
843 signature of the Sb-containing brake lining materials used in France during the decades.  
844 Preliminary data obtained on both solid and dissolved phases at the rural site indicate that  
845  $\delta^{123}\text{Sb}$  use as (bio)geochemical tracer is promising and should be further studied. Then, we  
846 show that Sb is subjected to important changes of speciation (oxidation state and ligands) in  
847 the road-to-pond waterway, and is thus highly sensitive to redox changes at the stormwater  
848 pond scale. To this respect, a perspective of research is to study the geochemical reactivity of  
849 Sb upon aging when the contaminated stormwater pond sediments are submitted to long  
850 period of dryness. Thus, mobility of Sb from the main Sb-bearing phases observed should be  
851 evaluated to help to manage this contamination. From the results presented here, we posit that  
852 the processes leading to speciation and isotopic modifications should be studied in details for  
853 a better management of Sb contamination in stormwater pond infrastructures and downstream  
854 aquatic environments, and subsequently in urban surface environments exposed to road traffic  
855 contaminations.

Journal Pre-proof

857 **Credit author statement**

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- 1141

<b>Denomination</b>	<b>GPS coordinates</b>	<b>Construction (year)</b>	<b>Type</b>	<b>Drained surface</b>	<b>Traffic per day (2017)</b>	<b>Presence of speed camera</b>
<b>Semi-urban, recent (SUR)</b>	48.7115, 2.1863	~2000	Decantation	Urban + Road	54,187	Yes
<b>Semi-urban, old (SUO)</b>	48.6334, 2.2246 48.6320, 2.2292	1990s	Decantation	Road	56,595	Yes
<b>Rural, recent (RR)</b>	48.5120, 1.9072 48.5125, 1.9082	2012	Decantation + filtration	Road	42,225	No

Highlights:

- Highway stormwater ponds concentrate Sb contamination from road runoff
- Sb isotopic composition of stormwater pond sediments is close to that of road dusts
- Sb(V)-O, Sb(III)-O, and Sb(III)-S species occur in the road-to-pond continuum
- Sb(III)-S species are observed as a specific signature of underwater reduced samples
- Sb speciation changes along the waterway show the high geochemical reactivity of Sb

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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