

# The ebullition of hydrogen, carbon monoxide, methane, carbon dioxide and total gaseous mercury from the Cornwall Area of Concern

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## Abstract

This paper reports the first ebullitive fluxes of hydrogen (H<sub>2</sub>), carbon monoxide (CO), methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>) and total gaseous mercury (TGM) from the Cornwall Area of Concern (CAC). Although sediments were contaminated with mercury, bubbling was a negligible source of mercury for the global atmosphere. Indeed, the average emission of TGM through ebullition was 0.04  $\mu\text{g m}^{-2} \text{h}^{-1}$ . Measurements of H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub> trapped gas concentrations and fluxes were used as indicators of diagenesis processes. The CAC represented a significant regional source of CH<sub>4</sub> since the estimated ebullitive fluxes (3.5  $\text{mg m}^{-2} \text{h}^{-1}$ ) were similar to the CH<sub>4</sub> emissions measured above typical flooded freshwater wetlands. As molecular diffusion is known as the main pathway of CO<sub>2</sub> transport from water to the atmosphere, CO<sub>2</sub> ebullitive fluxes were weak (0.39  $\text{mg m}^{-2} \text{h}^{-1}$ ). Bubbling of CO (1.6  $\mu\text{g m}^{-2} \text{h}^{-1}$ ) was 10 folds less important than CO fluxes measured over flooded freshwater wetlands. Finally, H<sub>2</sub> emissions (0.001  $\mu\text{g m}^{-2} \text{h}^{-1}$ ) were negligible since the level of this trace gas is tightly regulated by microorganisms in anaerobic environments.

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## 1. Introduction

The cycling of gases in the water column, and especially sediments, are important ecosystem processes (Huttunen et al., 2001). Trace gas emissions measured over aquatic environments are the sum of three

processes: molecular diffusion, ebullition and transport through emergent macrophytes. Among these three pathways, ebullition is an important mechanism in the release of gases from certain aquatic sediments (Chanton and Whiting, 1995). This mode of gas transport typically occurs in organic-rich, anoxic freshwater sediments, where anaerobic decomposition is the source of substantial gas production. Typically, the bubbles are consisting mainly of methane (CH<sub>4</sub>), nitrogen (N<sub>2</sub>), carbon dioxide (CO<sub>2</sub>) and other trace gases such as hydrogen (H<sub>2</sub>) and carbon monoxide (CO)

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(Chau et al., 1977). Bubbles may be released from the sediments through the water column to the atmosphere either spontaneously, or this can be triggered by some episodic events such as changes in air pressure, hydrostatic pressure (Mattson and Likens, 1990), wind activity (Upstill-Goddard et al., 1990) or seismic process (Tréhu et al., 1999).

The relative contribution of ebullition and molecular diffusion of gaseous species depends of their solubility in the water. Since  $\text{CH}_4$  is relatively insoluble, ebullition has been identified as a major process for its transport through the anaerobic sediments/water interface and may therefore play an important role in the release of potent greenhouse gases into the atmosphere (Brennwald et al., 2005; Shalini et al., 2006). In contrast,  $\text{CO}_2$  is an end-product of the respiration and is highly soluble in the water, leading often to an accumulation of high concentrations at depth.  $\text{CO}_2$  produced in oxygenated sediments may be consumed by photosynthesis or emitted to the atmosphere, predominantly by molecular diffusion since ebullition had no significance in its release from aquatic ecosystems (Casper et al., 2000; Huttunen et al., 2001). Sediments are also the source of other biogenic trace gases such as  $\text{H}_2$  and  $\text{CO}$  that are produced in anoxic conditions. Although  $\text{H}_2$  and  $\text{CO}$  are relatively insoluble in water, previous investigations suggested that plant-mediated transport was the main pathway for their emissions from anoxic sediments to the atmosphere (Conrad et al., 1988; Schütz et al., 1988).

Evolved gases characterization might be useful to study the sediment–water–air input to the global atmosphere and to infer the diagenesis processes in sediments. For instance,  $\text{CH}_4$  ebullitive fluxes are

indicators for labile organic matter decomposition rates and the oxidation state of the sediments (Casper et al., 2000; Shalini et al., 2006). Instead of being immediately emitted to the water column, newly formed  $\text{CH}_4$  bubbles are moving gradually in the sediments, leading to an increase of its diffusive flux (Rothfuss and Conrad, 1998). Due to their accumulation and movements,  $\text{CH}_4$  bubbles generated in mercury contaminated sediments may be enriched with gaseous mercury species.

This paper reports the ebullition concentrations and fluxes of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{CO}_2$  and TGM from the St. Lawrence River (Cornwall) Area of Concern (CAC). This section of the river was designated one of the Great Lakes Areas of Concern as a result of ecosystem degradation issues including mercury contamination of river bottom sediments resulting from long-term municipal and industrial discharges. Mercury ebullitive fluxes were negligible and unaffected by the oxidation state of the sediments. The absence of mercury emissions should be the result of its complexation by organic matters or reactions with iron, manganese and sulfur.

## 2. Methods

### 2.1. Locations

The Cornwall Area of Concern (CAC) includes a stretch of the St. Lawrence River approximately 80 km long, from the Moses–Saunders power dam to the eastern outlet of Lake St. François in Québec. Two site locations were selected for the purpose of this work (Fig. 1) and

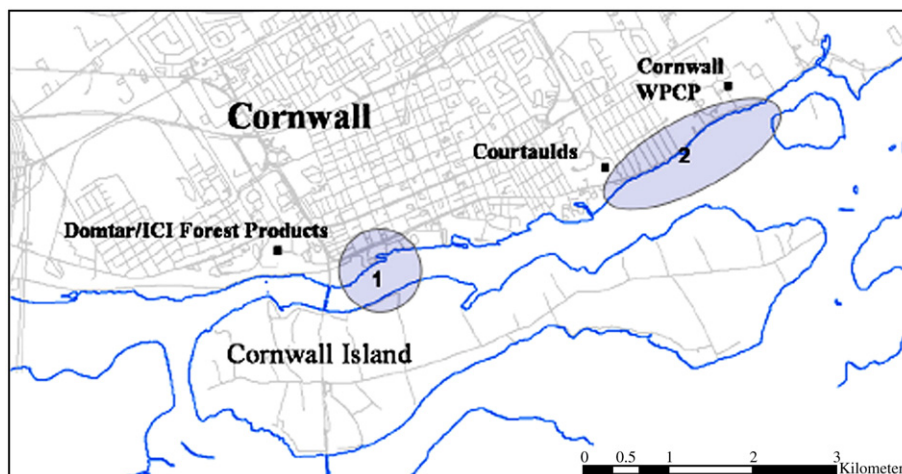


Fig. 1. Sampling location in Cornwall waterfront.

corresponded to two contamination zones in Cornwall vicinity (Richman and Dreier, 2001):

- 1) Zone 1: Lamoureux Park is the westernmost sampling location and immediately downstream of a pulp and paper mill.
- 2) Zone 2: Windmill Point to Pilon Island is the largest and easternmost zone, stretching from the former Courtaulds textile mill (operated until November 1992) to the eastern edge of Pilon Island.

## 2.2. Gas collection

The gas collector was in the form of a stainless steel cone fitted with large wide stainless steel feet placed away from the gas evolving area (Fig. 2). The cone collecting area was 2685 cm<sup>2</sup> and gases evolved from the sediments were collected by water displacement (Chau et al., 1977). Prior their deployment, gas collectors were washed with Citranox<sup>®</sup> detergent and methanol (ACS reagent grade). Collecting Teflon bottles were soaked 10 days in a 10% HNO<sub>3</sub> bath and rinsed with Milli-Q water before use. At the sampling site, the bottles were rinsed 3 times and filled with the lake water. On initial positioning of the cones, the cone was purged of gases by opening the valve fitting. The collectors were then fitted with a 500 mL Teflon<sup>®</sup> sample bottle connected to a fitting on top of the steel cone. The

sample bottle containing the gases were removed by SCUBA divers, capped and stored at 4 °C until analyses. Samples greater than 500 mL were collected by closing the valve fitting and replacing the filled collector bottle with a new bottle(s) until all of the gases collected inside the cone was released into the bottles.

Gas collectors were deployed at zone 1 in 10 m of water depth and in 3 m of water depth in zone 2 in July 2005. The bottom of these areas was flat with no vegetation. Over a 7 day period, 836 and 1000 ml of gas were respectively accumulated in the gas collectors at zone 1 and zone 2. Since the permeability of the Teflon<sup>®</sup> bottles for the measured trace gases have not been tested, concentrations and fluxes measured in that study might be underestimated, especially in the case of H<sub>2</sub> (Chapelle et al., 1997).

## 2.3. Gas analyses

Prior to the analyses, samples were allowed to equilibrate to room temperature at least for 60 min. The bottles were immersed in a Milli-Q water bath (Hg < 0.1 ng/L) to replace the storage cap for an injection port cap. The latter consisted to a Teflon cap equipped with an air tight injection port. Gas dilutions were performed before the analyses of CO, CH<sub>4</sub> and CO<sub>2</sub>.

### 2.3.1. H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub> concentrations measurements

Chromatographic RGA5 system (Trace Analytical, Maryland) was used for H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub> concentrations measurements. Two detectors were mounted in parallel: the reductive gas detector (RGD) for H<sub>2</sub> and CO and the flame ionization detector (FID) for CO<sub>2</sub> and CH<sub>4</sub>. Zero air (60–80 psig) was used for the general operation of the instrument (e.g. valves movements) and ultra high purity (UHP) nitrogen (30–70 psig) was employed as carrier gas. UHP hydrogen (20–40 psig) and zero air type vehicle emission (20–50 psig) supplied the ionizing flame of the FID.

Analyses were performed through direct injection of 10 mL of the sample in the injection port of the analyzer. An automated sample loop transferred 1 mL of the injected volume to the chromatographic columns. Each gas sample was analyzed 5 times, and analyses of blanks and calibration gas injections were done between each batch of sample. NOAA certified standard gas was used for the calibration (815 ppbv H<sub>2</sub>, 190.5 ppbv CO, 1875.8 ppbv CH<sub>4</sub> and 380.3 ppmv CO<sub>2</sub> in air).

### 2.3.2. Total gaseous mercury

The TGM analyses were achieved with an automatic analyzer (Tekran<sup>®</sup> 2537A). Briefly, the analytical train of

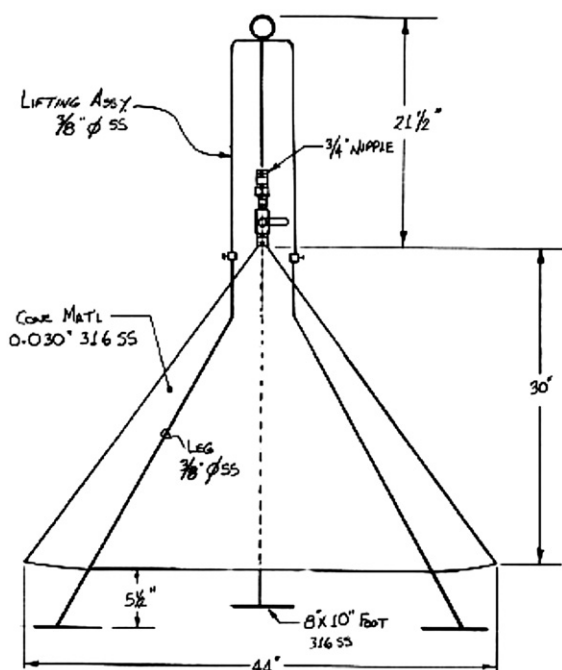


Fig. 2. Diagram of the gas collector utilized.

this instrument is based on the amalgamation of mercury onto a pure gold surface followed by a thermodesorption and analysis by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS) ( $\lambda=253.7$  nm) providing analysis of TGM in the air at sub-ng m<sup>-3</sup> levels. Analyses were performed through direct injection of 50 mL of the sample into the analyser. During the analyses, UHP grade zero air circulated through the Tekran® at a flowrate of 1.5 L min<sup>-1</sup>.

#### 2.4. Flux calculations

Trace gas fluxes ( $F(x)$ ) were derived with Eq. (1) where  $x$  is the trace gas concentration (ng m<sup>-3</sup> or  $\mu\text{g m}^{-3}$  or mg m<sup>-3</sup> for TGM or H<sub>2</sub>, CO or CH<sub>4</sub> and CO<sub>2</sub>, respectively),  $V$  is the total volume of the gas collected (m<sup>3</sup>),  $t$  is the time interval between the deployment of the gas collector (h) and  $S$  is the surface of the gas collector (m<sup>2</sup>)

$$F(x) = \frac{x \cdot V}{t \cdot S} \quad (1)$$

The conversions of H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub> concentrations from ppbv to  $\mu\text{g m}^{-3}$  were done by using Eq. (2) where  $x'$  is the trace gas concentration in ppbv, 0.0409 is the conversion factor (moles L<sup>-1</sup>) and MW is the molecular weight of the trace gas.

$$x = x' \cdot 0.0409 \cdot \text{MW} \quad (2)$$

### 3. Results and discussion

Mercury contamination of Cornwall sediments was first documented in 1970. An extensive sediment survey identified mercury contaminated sediment along the North Channel and extended almost 20 km downstream of the Cornwall waterfront (MOE, 1979). In order to restore and maintain the chemical, physical and biological integrity of the waters between Canada and the United States, the International Joint Commission has identified 42 areas of concern in the St. Lawrence River Basin. Among these sites, the Cornwall area of concern (CAC) is contaminated with mercury. Recent assessments have showed that total Hg concentrations in sediments were in the range of 0.79

to 1.71 and 0.44 to 19.5  $\mu\text{g g}^{-1}$  (dry weight) for zone 1 and zone 2, respectively (Richman and Dreier, 2001 and cited references). Although this contamination apparently came from two industrial point sources that closed their activities in the 1990s, the CAC may represent an important long-term source of mercury and carbon for the aquatic food chain and the atmosphere.

#### 3.1. Trace gas concentrations and fluxes

Reduced trace gases such as H<sub>2</sub>, CO and CH<sub>4</sub> are produced during the anaerobic degradation of organic matter. H<sub>2</sub> is one of the end-products generated during the fermentation of the organic matter while methanogenesis produces CH<sub>4</sub> and amounts of CO as intermediate metabolite. Methanogenesis is a terminal sink for electrons generated during the anaerobic degradation of organic matter and is important in the diagenesis of recently deposited sediments. The methanogenic *archaea* are known to proliferate in organic-rich sediments below the surface layer where oxygen penetration is limited. When traces of oxygen are present in the sediment surface, a significant proportion of the CH<sub>4</sub> may be oxidized to CO<sub>2</sub> (Segers, 1998 for a review). Importance of microbial CH<sub>4</sub> oxidation is well known in oxic–anoxic boundaries, such as the sediments upper layer, where less than 10% of the CH<sub>4</sub> produced in the sediments diffuses to the water column (Frenzel et al., 1990; Rothfuss and Conrad, 1998). In shallow lakes, CH<sub>4</sub> production rates are directly related to the rates of particulate carbon input to sediments (Rudd and Hamilton, 1978). As sedimentation rates of 2.6 and 0.8 cm yr<sup>-1</sup> were estimated for zone 1 and zone 2 (Rukavina, 2000), higher rates of CH<sub>4</sub> production were expected at the zone 1. Higher sedimentation rates for zone 1 likely reflect greater influences from industrial and municipal discharges in the Cornwall area than the downstream zone 2 site. Accordingly, the CH<sub>4</sub> content of the trapped gas was 30.7% for zone 1 and 22.7% for zone 2 (Table 1). Since the CH<sub>4</sub>/CO<sub>2</sub> concentration ratios were respectively 54 and 15 for zone 1 and zone 2, sediments of the zone 1 were the most anaerobic. Indeed, 3.1 fold more CO<sub>2</sub> was emitted from the sediments of zone 2 (Table 1). As a whole, bubble gas CH<sub>4</sub> and CO<sub>2</sub>

Table 1  
Concentrations and fluxes of hydrogen, carbon monoxide, methane, carbon dioxide and total gaseous mercury evolved from sediment

	[CH <sub>4</sub> ] (ppmv)	CH <sub>4</sub> flux (mg m <sup>-2</sup> h <sup>-1</sup> )	[CO <sub>2</sub> ] (ppmv)	CO <sub>2</sub> flux (mg m <sup>-2</sup> h <sup>-1</sup> )	[CO] (ppmv)	CO flux ( $\mu\text{g m}^{-2}$ h <sup>-1</sup> )	[H <sub>2</sub> ] (ppbv)	H <sub>2</sub> flux ( $\mu\text{g m}^{-2}$ h <sup>-1</sup> )	[TGM] (ng m <sup>-3</sup> )	TGM flux (pg m <sup>-2</sup> h <sup>-1</sup> )
Zone 1	307 848	3.73	5713	0.19	58	1.23	779	0.0012	2.55	0.047
Zone 2	227 164	3.30	14 858	0.59	81	2.06	591	0.0011	1.50	0.033

concentrations were typical and similar to levels measured in some hypereutrophic lakes (e.g., Huttunen et al., 2001).

In methanogenic sediments,  $H_2$  levels are tightly regulated.  $H_2$  is produced by fermenting bacteria and consumed by methanogenic *archaea* (Conrad, 1999). Since the fermenting bacteria are inhibited with high  $H_2$  concentrations, these bacteria form syntrophic association with methanogenic *archaea*. Release of  $H_2$  in gas bubbles from methanogenic sediments is therefore not expected. In freshwater lakes, the analysis of dissolved  $H_2$  concentrations vertical profiles showed that the diffusion of  $H_2$  from the sediments to the water column were negligible (Schütz et al., 1988). Indeed, more than 70% of the  $H_2$  was emitted via plant-mediated transport, while production in the water column and ebullition explained the remaining of the fluxes (Schütz et al., 1988). More recently,  $H_2$  concentrations in trapped bubbles of agitated submerged soil of natural wetlands varied from less than 1 to 205 ppmv (Sugimoto and Fujita, 2006). Accordingly, trapped gas  $H_2$  contents for both sampling sites (Table 1) were similar to the background tropospheric  $H_2$  concentration reported for the northern hemisphere (Novelli et al., 1999). Although  $H_2$  concentrations might be underestimated due to its diffusion through Teflon® walls of the collection bottles (Chapelle et al., 1997), the results suggest that ebullition from both zones represented an insignificant source of  $H_2$  for the atmosphere.

Previous works about CO emissions focused primarily on its photoproduction. Photodegradation of plants cellular material was proposed as a source of CO due to the lack of relationship between stomata conductance and CO emissions (e.g., Yonemura et al., 1999; Conrad et al., 1988). In a submerged rice field, vegetation rather than ebullition was the major contributor for CO emissions (Conrad et al., 1988). In boreal forest ponds, the dissolved CO concentrations followed a well-defined diurnal cycle with a supersaturation observed during daytime (Bourbonniere et al., 1997). Although photochemical reactions represent a significant source of CO to the atmosphere, microbial populations of the sediments unexposed to the sunlight might be important for the CO exchange between sediments and water column. For instance, the CO concentrations profile in deep sediments of Saanich Inlet (BC) provided the evidence that sediments represent a significant source of CO for the water column (Bird et al., 2001). Accordingly, trapped gas CO content reported in Table 1 are 1000 fold higher than the typical background level reported for CO in the troposphere of the northern hemisphere (Holloway et al., 2000). Although methanogenic, sulphate reducers

and acetogenic microorganisms possess the metabolic capacity to oxidize CO to  $CO_2$  in anaerobic conditions (Davidova et al., 1994; Mörsdorf et al., 1992), both zones acted as a CO source (Table 1).

Mercury (TGM) concentrations of evolved gas from sediments were larger in site 1 than site 2,  $2.55 \text{ ng m}^{-3}$  versus  $1.5 \text{ ng m}^{-3}$  respectively. The latter levels are similar to the typical TGM concentrations in the air (Poissant, 2000). The calculated TGM fluxes were negligible,  $0.047$  and  $0.033 \text{ pg m}^{-2} \text{ h}^{-1}$ , respectively for zone 1 and 2, compared with the photochemically-mediated production and evasion of TGM from the water column which was measured as  $330 \text{ pg m}^{-2} \text{ h}^{-1}$  for the upper St. Lawrence River (Poissant and Casimir (1998). These results suggest that mercury in the contaminated sediments of the CAC is mainly in non-volatile forms i.e. bonded to high molecular weight organic matter (Schuster, 1991; Skyllberg et al., 2000) associated to Fe and/or Mn oxo-hydroxides (Gobeil and Cossa, 1993; Canário et al., 2003) or under the form of cinnabar (HgS) (Morse, 1999).

Table 2

Trace gas ebullitive fluxes measured in other sites as well as net emissions measured over St. Lawrence River freshwater wetlands

Trace gas	Techniques	Flux	Sampling site
$CH_4$	Micrometeorological	$4.2 \text{ mg m}^{-2} \text{ h}^{-1}$	Flux measurements over a flooded freshwater wetland (Constant et al., 2005)
	Gas bubbling	$8 \text{ mg m}^{-2} \text{ h}^{-1}$	Gas bubbling in a small hypertrophic freshwater lake (Casper et al., 2000)
	Gas bubbling	$7.3 \text{ mg m}^{-2} \text{ h}^{-1}$	Gas bubbling in an estuarine river (Chanton and Martens, 1988)
$CO_2$	Micrometeorological	$1300 \text{ mg m}^{-2} \text{ h}^{-1}$	Flux measurements over a flooded freshwater wetland (Constant et al., 2005)
	Gas bubbling	$0.42 \text{ mg m}^{-2} \text{ h}^{-1}$	Gas bubbling in a small hypertrophic freshwater lake (Casper et al., 2000)
CO	Micrometeorological	$33 \text{ } \mu\text{g m}^{-2} \text{ h}^{-1}$	Flux measurements over a flooded freshwater wetland (Constant et al., 2005)
$H_2$	Micrometeorological	$42 \text{ } \mu\text{g m}^{-2} \text{ h}^{-1}$	Flux measurements over a flooded freshwater wetland (Constant et al., 2005)

### 3.2. Importance of the ebullition

Sediments bubbling at the CAC represented a significant localized source of CH<sub>4</sub>. For instance, CH<sub>4</sub> emissions of 4.2 mg m<sup>-2</sup> h<sup>-1</sup> were measured over a flooded freshwater wetland (Table 2) (Constant et al., 2005). Although sediments temperature and organic carbon content are important parameters influencing methanogenesis rates (Kelly and Chynoweth, 1981; Westermann, 1993), CH<sub>4</sub> ebullitive fluxes measured at the CAC were similar to other sites (Table 2). CO<sub>2</sub> ebullitive fluxes measured at the CAC were also in agreement with previous investigations (Table 2). Importantly, molecular diffusion, rather than the ebullition of CO<sub>2</sub> from sediments, accounts for 99% of the CO<sub>2</sub> emissions in freshwater lakes (Casper et al., 2000). CO<sub>2</sub> emissions measured over flooded freshwater wetlands were 1000 fold more important than the ebullitive fluxes derived at the CAC (Table 2). Although the CAC represented a source of CO for the atmosphere, the emissions were 10 folds less important than the CO fluxes measured over flooded freshwater wetlands (Table 2). This observation supports the idea that plant's cellular material and dissolved organic carbon photodegradations are the main sources of CO in aquatic ecosystems (Conrad et al., 1988). Finally, H<sub>2</sub> and TGM ebullitive fluxes were negligible. H<sub>2</sub> bubbling represented less than 0.002% of the H<sub>2</sub> emissions measured over submerged freshwater wetlands (Table 2). The average TGM air–water gas exchange in the Upper St. Lawrence River reported by Poissant and Casimir (1998) was 330 pg m<sup>-2</sup> h<sup>-1</sup>. Hence, the ebullition of TGM from sediments to water is a small contributor (less than 0.01%) to the TGM diffusion at the air–water interface and therefore is a minor contributor to the atmospheric mercury burden.

### 4. Conclusions

The results presented characterize ebullition of gases from two sediment deposition zones in the St. Lawrence River. It was shown that zones 1 and 2 are significantly distinct in term of sediment diagenesis, gas production and ebullition. Zone 1 was the most anaerobic area effective for the degradation of organic matter and the most important in the diagenesis of recently deposited sediments. Zone 1 is the most eutrophied zone in the CAC. Although the sediments of both sampled zone are contaminated with mercury (Richman and Dreier, 2001), the ebullition of TGM is not a significant contributor to the regional mercury burden compared with the river water column itself. Elemental mercury

formation following the reduction of ionic mercury by microorganisms (Mason et al., 1995) and photochemical reactions (e.g.: Amyot et al., 2000) are suggested as the major contributor for the mercury water–air exchanges through gas diffusion processes. Special attention should be given to zone 1 in terms of site remediation.

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