

# Chemical Risks Associated with Consumption of Shellfish Harvested on the North Shore of the St. Lawrence River's Lower Estuary

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Shellfish have the capacity to accumulate chemical contaminants found in their biotope and therefore present a potential risk for consumers. This study was conducted to assess the chemical risks associated with consumption of shellfish harvested on the north shore of the St. Lawrence River's lower estuary. A survey was carried out on 162 recreational harvesters, and shellfish were sampled for chemical contaminant analysis. We quantified 10 metals, 22 polycyclic aromatic hydrocarbons (PAHs), 14 polychlorinated biphenyls (PCBs), and 10 chlorinated pesticides. We subsequently evaluated cancer and noncancer risks for four consumption scenarios based on our survey results and published results. Soft-shell clams (*Mya arenaria*) were by far the most consumed shellfish species. Of the 56 selected contaminants, 36 were detected in the 23 homogenates of soft-shell clam meat. None of the contaminants found in the soft-shell clams were associated with intakes that exceed the main exposure limit recommendations proposed to prevent noncancer effects. However, several limits must be considered before drawing conclusions about the relative safety of shellfish consumption regarding this end point. Furthermore, inorganic arsenic and PCBs were present in sufficient concentrations to lead to cancer risks exceeding the level often considered acceptable for environmental exposure ( $1 \times 10^{-4}$  to  $1 \times 10^{-6}$ ) in each of the four scenarios, even for the lowest observed scenario of 15 meals of soft-shell clams per year. **Key words:** cancer risks, chemical, contamination, inorganic arsenic, PCBs, polychlorinated biphenyls, shellfish. *Environ Health Perspect* 112:883–888 (2004). doi:10.1289/ehp.6847 available via <http://dx.doi.org/> [Online 10 March 2004]

Many residents on the north shore of the St. Lawrence River's lower estuary harvest and eat bivalve shellfish found in this territory. They therefore ingest the various contaminants contained in these organisms. Although the shellfish and shellfish-harvesting areas are regularly inspected in order to detect the presence of toxic algae or microbiologic contamination, the existing monitoring program does not include the characterization of chemical contamination in this region.

Bivalve shellfish are marine invertebrates known to be reliable indicators of the marine environment (Cossa 1989; Goldberg et al. 1978; Ramade 1992). In fact, they present several characteristics of a "bioindicator" organism: sedentariness, capacity to bioaccumulate contaminants without being affected by them, accessibility, and longevity. In addition, the contamination rate of these organisms correlates directly with the biotope contamination level.

Such considerations also make consumption of shellfish potentially dangerous to human health. To better estimate and control such a risk, it has been recommended that a program be set up to estimate shellfish consumption, to identify populations at high risk, and to determine the distribution, nature, and extent of residues in the various marine organisms (Dawe et al. 1991).

The present study was carried out in order to accurately document the shellfish consumption of recreational harvesters of the north shore of the St. Lawrence River's lower estuary.

In addition, we analyzed samples of shellfish harvested in this area to determine the nature and levels of the chemical contamination. We also aimed to assess the cancer and noncancer risks associated with consumption of shellfish harvested in this area.

## Materials and Methods

**Study population.** The population studied was the group of recreational shellfish harvesters living on the north shore of the St. Lawrence River's lower estuary. This region extends from Tadoussac to Baie-Trinité and therefore covers 365 km of shoreline. In 2001, close to 48,000 people lived in this area. Recreational shellfish harvesters were met at 18 harvesting areas identified as frequently visited.

**Evaluation of shellfish consumption habits.** The shellfish consumption habits of the studied population were evaluated in two ways. First, the harvesters were surveyed on shores during periods suitable for harvesting, namely, 2- to 3-hr periods in which the intertidal zone was accessible. Besides being conducted in a relaxed atmosphere, this type of investigation allowed participants to continue to harvest shellfish while answering questions. The survey was conducted using a semistructured interview guide. This approach was validated on other health issues related to the St. Lawrence such as fish consumption, drinking water, and swimming (LaRue A. et al. 1996; LaRue and Grondin 1995; LaRue R. et al. 1996). Each interview took approximately 15 min and included questions on harvesting

frequency, shellfish harvesting experience, the species particularly sought, and the number of shellfish meals consumed in the last week and in the last year. Most of the shellfish-harvesting areas selected were visited twice in order to maximize the number of harvesters surveyed.

Second, the harvesters who answered the questionnaire were asked to complete a food diary during the 30 days after the survey. They were asked to record every shellfish meal, including the date, the type and origin of the shellfish, and the amount of shellfish consumed per person.

**Shellfish sampling areas.** Of the 18 harvesting areas selected for the survey, 8 were selected for shellfish sampling for chemical contaminant analysis. The selection of sampling areas was based on the number of harvesters and the presence of point and diffuse sources of chemical pollution nearby. A description of these sources of pollution is presented in Table 1.

**Shellfish sampling and homogenate preparation.** Sampling was performed during the spring. In each sampling area, we sampled the quantity of specimens needed (about 30) to prepare three homogenates of 200 g meat. Soft-shell clams were harvested using a shovel or a spade; the shellfish were then placed in a plastic pail and subsequently transferred to a cooler filled with ice cubes. The shellfish were shelled and washed in distilled water to remove salt and sand. The meat was then ground, homogenized, and stored in a freezer at  $-20^{\circ}\text{C}$  until it was transported by plane to the laboratory.

**Selected contaminants.** The contaminants chosen for the chemical risk assessment were selected because *a*) they are likely to bioaccumulate in the marine invertebrates of the study area; *b*) they have suspected or recognized harmful effects; and *c*) their presence is relatively constant in the environment. These contaminants were divided into two categories: metals (or metalloids) and organic compounds.

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We quantified 10 metals, 22 polycyclic aromatic hydrocarbons (PAHs), 14 polychlorinated biphenyl (PCB) congeners [congener numbers from the International Union for Pure and Applied Chemistry (IUPAC)], and 10 chlorinated pesticides. The selected contaminants are presented in Table 2.

We studied the following arsenic species: trivalent arsenic (As<sup>+3</sup>), pentavalent arsenic (As<sup>+5</sup>), dimethylarsinic acid (DMA), and monomethylarsonic acid, as well as arsenobetaine and arsenocholine, two forms of dietary arsenic.

**Chemical analysis.** Metals and organic compounds were analyzed by the toxicology laboratory of the Institut National de Santé Publique du Québec, the former Quebec Toxicology Center, Quebec City, Canada. This laboratory is accredited under ISO 17025 by the Standards Council of Canada and participates in several external quality assurance programs. Internal quality assurance procedures include standard calibration curve, blanks, reference materials, and 10% of duplicates.

For the metal determination, 1 g (wet weight) of shellfish homogenate was digested with 2 mL ultrapure nitric acid for 16 hr at 120°C in a closed vessel. Mercury was determined using the cold vapor generation method (Ebbestad et al. 1975). All other metals were determined by inductively coupled plasma mass spectrometry (ICP-MS; Elan 5000; Perkin-Elmer Sciex Instruments, Concord, Ontario, Canada).

Speciation of the various forms of arsenic was done on the seven homogenates with the highest arsenic concentrations. The homogenates were incubated at 37°C for 12 hr and centrifuged for 20 min to separate the aqueous and solid phases. The supernatant obtained was then filtered on 2.5- and 0.45-µm membranes, and the filtrate was diluted with the HPLC system's mobile phase. Chromatography was carried out by ion pairing using a ZORBAX C<sub>18</sub> column (Chromatograph Specialties Inc., Brockville, Ontario, Canada), and ICP-MS was used for detection (Zbinden et al. 2000).

Organic compound analyses were performed on 8 g (wet weight) of homogenate.

**Table 1.** Description of point and diffuse sources of chemical contamination present in the areas chosen for shellfish sampling.

Origin	Type
Point sources	Dump
	Sawmill
	Pulp and paper plant
	Hydroelectric power station
	Aluminum smelter
	Port facilities
	Untreated and treated municipal wastewater
Diffuse sources	Residential septic installations
	Agricultural runoff

PCB congeners and chlorinated pesticides were extracted using dichloromethane and anhydrous sodium sulfate. Before being filtered on sodium sulfate, the organic fraction was washed with distilled water. The organic solvent was then concentrated by evaporation to 1.2 mL. Extracts were then purified on Florisil before being analyzed by a gas-phase chromatograph equipped with an electron capture detector (adapted from Patterson et al. 1986).

PAH analyses were performed using 4 g (wet weight) of homogenate. The PAHs were extracted using dichloromethane. The organic fraction was washed with distilled water and concentrated by evaporation to 1.5 mL. These extracts were concentrated and separated by gas-phase chromatography on a 30-m capillary column (HP-5MS; Agilent, Wilmington, DE, USA). Finally, identification and quantification were done by a mass spectrometer in sequential selective ion monitoring mode [adapted from U.S. Environmental Protection Agency (EPA) Method 8270B (U.S. EPA 1994)].

**Concentrations calculated.** If a contaminant's concentration was below the detection threshold, we used a concentration equal to half of the detection limit in calculations of

mean concentrations. The SD, median, and 95th percentile were also calculated. Total PCB concentrations were quantified with an Aroclor-based method and expressed in terms of Aroclor 1260. Aroclor was the trade name of a PCB technical mixture that was sold in North America; Aroclor 1260, with Aroclor 1254 and 1242, made up the bulk of production (Sather et al. 2001). Aroclor 1260 has been estimated to be 5.2 times the sum of PCB congeners 138 and 153 (Nadon et al. 2002). Total chlordane concentration was calculated by adding the concentrations of  $\alpha$ -chlordane,  $\gamma$ -chlordane, *cis*-nonachlor, oxychlordane, and *trans*-nonachlor.

**Estimation of contaminant intakes.** We estimated daily intakes by multiplying the 95th percentile of the contaminant concentration by the daily shellfish consumption estimated using the results of the survey and food diaries. The result was then divided by the weight of an average Canadian adult (70 kg) to obtain a dose expressed as micrograms per kilogram per day. For arsenic, we assumed that 10% of the total concentration contained in the shellfish was inorganic as estimated by the U.S. Food and Drug Administration (FDA 1993).

**Table 2.** Categories of selected contaminants.

Category	Contaminant
Metals and metalloids	Arsenic <sup>a</sup> , mercury, selenium, cadmium, nickel, zinc, chromium, lead, copper, manganese
Organic compounds	PCBs: IUPAC congeners 28, 52, 99, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183, 187 PAHs: naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo( <i>c</i> )phenanthrene, benzo( <i>a</i> )anthracene, chrysene, benzo( <i>b,k</i> )fluoranthene, benzo( <i>a</i> )anthracene, benzo( <i>e</i> )pyrene, benzo( <i>a</i> )pyrene, methylchloranthrene, indeno(1,2,3- <i>cd</i> )pyrene, dibenzo( <i>a,h</i> )anthracene, benzo( <i>g,h,i</i> )perylene, dibenzo( <i>a,l</i> )pyrene, dibenzo( <i>a,i</i> )pyrene, dibenzo( <i>a,h</i> )pyrene Chlorinated pesticides: mirex, $\alpha$ -chlordane, $\gamma$ -chlordane, <i>cis</i> -nonachlor, oxychlordane, <i>trans</i> -nonachlor, hexachlorobenzene, <i>p,p'</i> -DDT, <i>p,p'</i> -DDE, lindane

DMA, dimethylarsenic acid.

<sup>a</sup>Various forms analyzed: total As, As<sup>+5</sup>, As<sup>+3</sup>, monomethylarsenic acid, DMA, arsenobetaine, and arsenocholine.

**Table 3.** Descriptive results of the survey carried out on 162 harvesters.

Item	Category	Percent (n/N)
Age (years)	≤ 20	5.6 (9/160)
	20–34	31.9 (51/160)
	35–49	43.1 (69/160)
	≥ 50	19.4 (31/160)
Shellfish harvesting frequency	< 3 times/year	38.9 (63/162)
	A few times/year	14.2 (23/162)
	Many times/month	46.9 (76/162)
Shellfish harvesting experience (years)	≤ 2	16.2 (24/148)
	2–5	13.5 (20/148)
	> 5	70.3 (104/148)
Preferred shellfish species <sup>a</sup>	Soft-shell clam <sup>b</sup>	95.2 (138/145)
	Common northern whelk <sup>c</sup>	22.8 (33/145)
	Blue mussel <sup>d</sup>	17.2 (25/145)
	Common periwinkle <sup>e</sup>	2.8 (4/145)
	Arctic wedge clam <sup>f</sup>	1.4 (2/145)
	Other species	2.1 (3/145)
Number of shellfish meals in the previous year	< 5	35.1 (52/148)
	5–10	19.6 (29/148)
	11–20	15.5 (23/148)
	> 20	29.7 (44/148)

Abbreviations: n, number of mentions; N, number of shellfish harvesters who answered the question.

<sup>a</sup>More than one answer possible. <sup>b</sup>*Mya arenaria*. <sup>c</sup>*Buccinum glaciale*. <sup>d</sup>*Mytilus edulis*. <sup>e</sup>*Littorina*. <sup>f</sup>*Mesodesma arctatum*.

**Risk assessment.** We evaluated two types of health effects in this study: cancer and noncancer effects. Noncancer risk assessment was performed for contaminants for which an exposure limit recommendation was proposed by the U.S. EPA, the Agency for Toxic Substances and Disease Registry (ATSDR), the World Health Organization (WHO), or Health and Welfare Canada (HWC). Risks were estimated by comparing the calculated contaminant intakes with the exposure limit recommended. For cancer effects, we evaluated risks for substances classified as a human carcinogen (category A) or probable human carcinogen (categories B1, B2) by the U.S. EPA (2003a) and for which a slope factor was available specifically for oral exposure. Cancer risks were evaluated by multiplying the contaminant intakes with the slope factors proposed by the U.S. EPA in the Integrated Risk Information System (IRIS) database (U.S. EPA 2003a). Cancer and noncancer risk assessments were limited to single contaminants that were detected in  $\geq 70\%$  of the homogenates.

## Results

**Consumption habits.** During the investigation, 162 shellfish harvesters were surveyed. Descriptive results of this survey are presented in Table 3. Almost half (46.9%) said that they

harvested shellfish many times each month, and most (70.3%) had shellfish harvesting experience of  $> 5$  years. Of the participants, 95.2% said they gathered soft-shell clams (*Mya arenaria*); this species is by far the most preferred. Nearly one harvester in three (33.1%) gathered and ate more than one species of marine invertebrate. An average consumption frequency of 15 meals of shellfish per year could be obtained by multiplying the median obtained for each of the annual consumption frequency categories presented in Table 3 (35 meals in the  $> 20$  category; data not shown) by the percentage of harvesters in each of these categories.

Of the 162 shellfish harvesters met, 24 filled out and returned their food diary to the investigators. This allowed 90 shellfish meals to be described. Two-thirds (65.6%) of these meals consisted of soft-shell clams. As recorded in the food diaries, the shellfish harvesters consumed 47 shellfish (arithmetic mean) at each meal. Assuming that the shellfish consumed were always soft-shell clams, this value can be multiplied by the average wet weight of a clam (estimated in this study at 8.7 g) to determine the average quantity of meat consumed at each meal, or 410 g.

**Consumption scenarios.** We established four consumption scenarios for shellfish

harvesters. The first two scenarios were based directly on the results obtained in our survey. The remaining scenarios were based on consumption data found in the literature and represent consumption profiles whose existence can be anticipated in the study area.

The first scenario is based on the average quantity of shellfish consumed at each meal, or 410 g wet weight, and on the average consumption frequency of shellfish meals, established as 15 meals/year. The product of these two values gives an annual shellfish consumption of 6.2 kg, or the equivalent of an average daily consumption of approximately 17 g of shellfish.

The second scenario targets harvesters who are regular consumers of shellfish. It is based on an annual consumption frequency of 35 meals, the median of the annual consumption frequency for the  $> 20$  category, and applies to 30% of the population studied (Table 3). When this value is multiplied by the average quantity of shellfish meat consumed at each meal, 410 g, the annual consumption for these harvesters is 14.6 kg and the daily consumption is 40 g.

The third scenario represents the consumption of harvesters who eat shellfish regularly, based on its abundance and its accessibility. We therefore assumed that these people replaced meat and poultry with shellfish

**Table 4.** Results of metal analysis in 23 soft-shell clam homogenates.

Metal	Mean $\pm$ SD <sup>a</sup> ( $\mu\text{g/g}$ )	Median ( $\mu\text{g/g}$ )	95th percentile ( $\mu\text{g/g}$ )	Range ( $\mu\text{g/g}$ )	Detection limit ( $\mu\text{g/g}$ )	Percent positive for compound
Arsenic <sup>a</sup>	0.82 $\pm$ 0.14	0.79	1.04	0.57–1.08	0.10	100
Cadmium	0.05 $\pm$ 0.01	0.05	0.07	0.03–0.08	0.01	100
Chromium	0.46 $\pm$ 0.15	0.45	0.75	0.26–0.78	0.10	100
Copper	1.21 $\pm$ 0.27	1.21	1.57	0.69–1.8	0.01	100
Lead	0.09 $\pm$ 0.08	0.06	0.21	0.03–0.43	0.03	100
Manganese	5.2 $\pm$ 2.76	4.53	9.71	1.44–9.81	0.01	100
Mercury	0.01 $\pm$ 0.01	0.01	0.02	0.005–0.028	0.01	100
Nickel	0.30 $\pm$ 0.11	0.28	0.50	0.12–0.53	0.05	100
Selenium	0.34 $\pm$ 0.05	0.33	0.42	0.24–0.43	0.1	100
Zinc	10.38 $\pm$ 1.46	10.58	12.61	7.2–12.65	0.01	100

Concentrations are given in wet weight.

<sup>a</sup>Arithmetic mean. <sup>b</sup>Total arsenic (inorganic and organic).

**Table 5.** Results of organic compound analysis in 23 soft-shell clam homogenates.

Compound	Mean <sup>a</sup> $\pm$ SD ( $\mu\text{g/g}$ )	Median ( $\mu\text{g/g}$ )	95th percentile ( $\mu\text{g/g}$ )	Range ( $\mu\text{g/g}$ )	Detection limit ( $\mu\text{g/g}$ )	Percent positive for compound
PCB-52	0.10 $\pm$ 0.10	0.06	0.29	ND–0.36	0.03–0.04	96
PCB-99	0.06 $\pm$ 0.04	0.05	0.13	ND–0.15	0.03–0.04	87
PCB-101	0.10 $\pm$ 0.10	0.06	0.30	ND–0.41	0.03–0.04	96
PCB-105	0.09 $\pm$ 0.08	0.06	0.24	ND–0.30	0.03–0.04	96
PCB-118	0.10 $\pm$ 0.08	0.06	0.26	ND–0.32	0.03–0.04	96
PCB-138	0.12 $\pm$ 0.09	0.10	0.30	0.03–0.37	0.03–0.04	100
PCB-153	0.15 $\pm$ 0.09	0.12	0.33	0.04–0.43	0.03–0.04	100
PCB-187	0.08 $\pm$ 0.05	0.06	0.18	0.08–0.18	0.03–0.04	100
Naphthalene	8.42 $\pm$ 1.33	8.5	10.75	6.6–11.0	2.0	100
Benzo(e)pyrene	2.63 $\pm$ 2.41	1.85	5.78	ND–11.0	1.0	74
$\alpha$ -Chlordane	0.05 $\pm$ 0.02	0.05	0.08	ND–0.11	0.03–0.04	78
trans-Nonachlor	0.04 $\pm$ 0.02	0.04	0.07	ND–0.11	0.03–0.04	70
Hexachlorobenzene	0.15 $\pm$ 0.09	0.14	0.25	0.05–0.5	0.03–0.04	100
p,p'-DDE	0.2 $\pm$ 0.08	0.18	0.30	0.08–0.45	0.03–0.04	100
p,p'-DDT	0.12 $\pm$ 0.06	0.11	0.23	0.05–0.3	0.07	100

ND, not detected. Concentrations are given in wet weight.

<sup>a</sup>Arithmetic mean.

every second day. Because the average quantity of meat and poultry consumed by Canadians is approximately 112 g/day (Statistics Canada 2002), replacement by shellfish every second day would result in an average daily consumption of 56 g of shellfish.

The final scenario assumes extreme consumption and uses the value of the 99th percentile of the daily consumption of shellfish reported in the United Kingdom (WHO 1985), which is 95 g.

**Contaminant concentrations.** We detected 36 of the 56 selected contaminants. Results of analysis of all meat homogenates (one homogenate was lost) are presented in Tables 4 and 5. Results were available for 23 homogenates, not 24 as expected, because in one of the eight sampling areas, the number of shellfish sampled allowed only two homogenates to be prepared instead of three. Results presented are limited to contaminants that were detected in 70% of the homogenates. Considering that most shellfish consumed were soft-shell clams, only the results for this species are presented here. Contaminant concentrations are expressed as wet weight, with the average percentage of water in soft-shell clams being 88.4%.

All metals of interest were detected in each of the 23 homogenates analyzed. Arsenic speciation revealed that 8.2% of total concentration was inorganic, with values ranging from 1.8% to 19%. The organic compounds that were detected in each of the homogenates were PCB-138, PCB-153, PCB-187, naphthalene, hexachlorobenzene, *p,p'*-dichlorodiphenyltrichloroethane (*p,p'*-DDT), and *p,p'*-dichlorodiphenyldichloroethylene (*p,p'*-DDE).

**Chemical risks.** The contaminant intakes associated with the various consumption scenarios are shown in Table 6. We assumed that all the consumed shellfish were soft-shell

clams. These intakes never exceeded the most conservative exposure limit recommendations proposed to prevent noncancer effects. Cancer risks were evaluated for PCBs, inorganic arsenic, chlordanes, hexachlorobenzene, *p,p'*-DDE, and *p,p'*-DDT. The cancer risks associated with the four scenarios are presented in Table 7. The presence of inorganic arsenic and PCBs may lead to a cancer risk  $> 1 \times 10^{-6}$  for daily consumption of soft-shell clam meat of  $\geq 17$  g.

## Discussion

Results of the present study suggest that the consumption of harvested shellfish does not represent a significant risk of noncancer effects to the consumer's health. However, several limits must be considered before drawing conclusions about the relative safety of shellfish consumption regarding this end point. First, not all harvesting areas were sampled, and the sample size was small for each selected area. Second, for a few dietary assessments, the high-end exposure is close to the most conservative exposure limit available (e.g., inorganic arsenic, cadmium, chromium). Third, exposure limits recommended are not necessarily that conservative (Hattis et al. 2002). Fourth, using a body weight of 70 kg for contaminant intake estimations in adults necessarily underestimated the intakes and risks for children,

because they eat three to four times more food in proportion to their body size than do adults and therefore ingest larger amounts of chemicals per unit of body mass (U.S. EPA 2003b). Finally, some of the contaminants do not have detectable thresholds (e.g., lead).

For cancer effects, risks assessments related to PCBs and inorganic arsenic were  $> 1 \times 10^{-6}$ , even for the first exposure scenario. The U.S. EPA generally considers an excess upper-bound lifetime cancer risk to an individual of between  $10^{-4}$  and  $10^{-6}$  as an acceptable range (U.S. EPA 1999a, 1999b, 2001), meaning that regular exposure to a substance would lead to less than one case of cancer per 10,000 or 1,000,000 exposed persons. Our results therefore reveal an elevated cancer risk associated with soft-shell clam consumption in the area studied.

Seafood is recognized as one of the main dietary sources of arsenic (Muñoz et al. 2000; Suñer et al. 1999). However, arsenic found in shellfish is generally considered nontoxic because it is present in its organic form; only the inorganic forms, arsenite ( $As^{+3}$ ) and arsenate ( $As^{+5}$ ), are considered toxic. Nonetheless, although the forms of arsenic found in greater quantity in these organisms are arsenobetaine and the arsenosugars (Li et al. 2003), the fact remains that these organisms may contain a nonnegligible proportion of inorganic arsenic,

**Table 7.** Lifetime cancer risk associated with each consumption scenario.

Contaminant	Slope factor <sup>a</sup> (per mg/kg/day)	Consumption scenarios (g/day)			
		17	40	56	95
Total PCBs	2.00 <sup>b</sup>	$1.59 \times 10^{-6}$	$3.74 \times 10^{-6}$	$5.24 \times 10^{-6}$	$8.89 \times 10^{-6}$
Inorganic arsenic	1.50	$3.75 \times 10^{-5}$	$8.85 \times 10^{-5}$	$1.25 \times 10^{-4}$	$2.10 \times 10^{-4}$
Chlordane	0.35	$2.72 \times 10^{-9}$	$6.40 \times 10^{-9}$	$8.96 \times 10^{-9}$	$1.52 \times 10^{-7}$
Hexachlorobenzene	1.60	$9.87 \times 10^{-9}$	$2.32 \times 10^{-7}$	$3.25 \times 10^{-7}$	$5.52 \times 10^{-7}$
<i>p,p'</i> -DDE	0.34	$2.48 \times 10^{-9}$	$5.81 \times 10^{-9}$	$8.16 \times 10^{-9}$	$1.38 \times 10^{-7}$
<i>p,p'</i> -DDT	0.34	$1.90 \times 10^{-9}$	$4.47 \times 10^{-9}$	$6.26 \times 10^{-9}$	$1.06 \times 10^{-7}$

<sup>a</sup>Data from U.S. EPA (2003). <sup>b</sup>Upper-bound slope factor for food chain exposure.

**Table 6.** Contaminant intakes ( $\mu\text{g}/\text{kg}/\text{day}$ ) associated with each of the shellfish consumption scenarios.<sup>a</sup>

Contaminant	Consumption scenario (g/day)				Most conservative exposure limit
	17	40	56	95	
Arsenic (inorganic)	0.025	0.059	0.083	0.14	0.3 <sup>b,c</sup>
Cadmium	0.017	0.040	0.056	0.095	0.20 <sup>c</sup>
Chlordane (total)	$7.77 \times 10^{-5}$	$1.83 \times 10^{-4}$	$2.56 \times 10^{-4}$	$4.34 \times 10^{-4}$	0.05 <sup>e</sup>
Chromium	0.18	0.43	0.6	1.01	3.00 <sup>b</sup>
Copper	0.38	0.90	1.256	2.13	250.00 <sup>e</sup>
Hexachlorobenzene	$6.17 \times 10^{-5}$	$1.71 \times 10^{-4}$	$2.03 \times 10^{-4}$	$3.45 \times 10^{-4}$	0.05 <sup>c</sup>
Lead	0.05	0.12	0.168	0.28	3.50 <sup>d</sup>
Manganese	2.36	5.55	7.768	13.18	140.00 <sup>b</sup>
Mercury	$5.83 \times 10^{-3}$	0.014	0.019	0.033	0.71 <sup>d</sup>
Naphthalene	$2.62 \times 10^{-3}$	$6.17 \times 10^{-3}$	$8.64 \times 10^{-3}$	$1.47 \times 10^{-2}$	20.00 <sup>b,c</sup>
Nickel	0.12	0.29	0.4	0.68	5.00 <sup>d</sup>
PCBs (total)	$7.96 \times 10^{-4}$	$1.87 \times 10^{-3}$	$2.62 \times 10^{-3}$	$4.45 \times 10^{-3}$	0.02 <sup>c</sup>
<i>p,p'</i> -DDE	$7.29 \times 10^{-5}$	$1.71 \times 10^{-4}$	$2.4 \times 10^{-4}$	$4.07 \times 10^{-4}$	0.50 <sup>c</sup>
<i>p,p'</i> -DDT	$5.59 \times 10^{-5}$	$1.31 \times 10^{-4}$	$1.84 \times 10^{-4}$	$3.12 \times 10^{-4}$	0.50 <sup>c</sup>
Selenium	0.10	0.24	0.336	0.56	5.00 <sup>b,c</sup>
Zinc	3.06	7.21	10.088	17.11	300.00 <sup>b,c</sup>

Abbreviations: ADI, acceptable daily intake; MTDI, maximum tolerable daily intake; PTMDI, provisory tolerable maximum daily intake; pTDI, provisional tolerable daily intake; TDI, tolerable daily intake.

<sup>a</sup>Assuming that the shellfish consumed are always soft-shell clams. <sup>b</sup>Oral reference dose; data from U.S. EPA (2003). <sup>c</sup>Oral intermediate or chronic minimal risk level; data from ATSDR (2003). <sup>d</sup>ADI/TDI/PTMDI; data from WHO (1985). <sup>e</sup>ADI/pTDI/MTDI; data from HWC (1985).

with this fraction increasing with the level of environmental contamination.

Our results revealed that shellfish may contain a relatively large amount of inorganic arsenic (up to 19% of the total arsenic in one homogenate). Because the mean proportion of inorganic arsenic we found (8.2%) and the value proposed by the FDA (10%) are comparable, we used this latter value in our dietary intake calculations because it is less subject to experimental errors.

The mean concentration we obtained for inorganic arsenic,  $0.097 \mu\text{g/g}$  wet weight, is comparable with published values of  $0.103 \pm 0.043 \mu\text{g/g}$  and  $0.137 \pm 0.42 \mu\text{g/g}$  reported for mussels (*Mytilus edulis*) (Buchet et al. 1996), which is significantly greater than published values for clams,  $0.014 \pm 0.02 \mu\text{g/g}$  (Li et al. 2003). The mean concentration of inorganic arsenic as dry weight,  $0.8342 \mu\text{g/g}$ , is approximately 2.3 times greater than that found in a group of bivalve shellfish ( $0.36 \mu\text{g/g}$ ) (Muñoz et al. 2000). However, it is important to note that shellfish purchased in supermarkets, like those analyzed in these studies, are usually inspected for microbiologic and chemical contamination and then sold, in contrast to the organisms considered in the present study.

Inorganic arsenic has been identified as a group A human carcinogen (carcinogenic to humans) by the U.S. EPA (2003a). Numerous epidemiologic studies demonstrate that the ingestion of inorganic arsenic in drinking water increases the incidence of skin, bladder, and lung cancer, with the internal cancers considered the main cancers of concern [National Research Council (NRC) 2001]. Inorganic arsenic in shellfish therefore presents a potential health risk for shellfish harvesters.

There is no consensus regarding the quantity of inorganic arsenic that is absorbed after seafood consumption. In one study Buchet et al. (1969) concluded that this amount is not biologically significant. However, in that study, the excretion of inorganic arsenic for regular seafood consumers was greater than that for those who never eat seafood, a difference that was statistically significant.

Even though the nontoxic characteristic of arsenobetaine, excreted rapidly without being metabolized, has been demonstrated numerous times (Sabbioni et al. 1991), the effects of the arsenosugars still remain to be clarified. In fact, recent studies have demonstrated the presence of DMA, dimethylarsinoethanol, trimethylarsine oxide, and numerous metabolites, whose nature and toxicity are still unknown, in the urine of people who have consumed arsenosugars (Francesconi et al. 2002; Le et al. 1999). These results reveal that arsenosugars are not only biotransformed after their ingestion but also could have a toxic potential. We did not measure arsenosugars in

the present study, but research demonstrates that they are one of the two most abundant forms of arsenic in shellfish (Li et al. 2003). In addition, the important cytotoxic and genotoxic characteristic of the intermediate trivalent metabolites produced in the formation of DMA and trimethylarsine oxide from inorganic arsenic was recently proven (Mass et al. 2001; Styblo et al. 2000). Because these studies demonstrate the toxic potential of the other forms of arsenic found in shellfish, they also challenge the consensus regarding nontoxicity of the arsenic found in marine invertebrates.

Furthermore, the cancer risk associated with inorganic arsenic was estimated in our study with the slope factors proposed in the IRIS database (U.S. EPA 2003a), but the dose–response models used by the U.S. EPA for cancer risk give estimates lower than the estimates made by the NRC (2001).

For total PCBs, the mean concentration obtained in our study ( $1.40 \times 10^{-3} \mu\text{g/g}$ ) is of the same order of magnitude as the mean concentrations of  $4.59 \times 10^{-3} \mu\text{g/g}$  measured in Europe in clams (Binelli and Provini 2003) but is significantly less than the value of  $1.51 \times 10^{-1} \mu\text{g/g}$  measured in Quincy Bay, Massachusetts (Cooper et al. 1991); this possibly reveals a variation in the contamination levels of the locations where the shellfish were harvested.

In the present study, we found that PCBs found in shellfish were also associated with an excessive cancer risk. The method we used to determine total PCBs in the present cancer risk assessment was based on Aroclor. For low-trophic-level samples such as clam and mussel samples, this method has been shown to be equivalent to a mixing model that uses the full congener data (Sather et al. 2003). PCBs are classified as group B2 (probable human carcinogen) by the U.S. EPA (2003a).

Mirex, lindane, and most of the PAHs could not be detected in the homogenates we analyzed. The use of mirex was prohibited in the United States in the 1970s (O'Connor 1998), and its concentration in the environment has dropped since that time. However, the failure to detect a specific contaminant in shellfish does not mean that this contaminant is not present in the environment. This raises the question of detection limit levels and the consequences of limiting the risk assessment to contaminants that were detected in a certain proportion of samples (e.g., 70%). For example, if all the homogenates contained benzo(a)pyrene just below the detection limit of  $1 \mu\text{g/kg}$ , the associated cancer risk would be close to  $1.77 \times 10^{-6}$  for a daily intake of 17 g of soft-shell clam meat and  $9.9 \times 10^{-6}$  for a daily intake of 95 g. This demonstrates that if the detection limit is relatively high, the cancer risk could be underestimated. However, choosing to consider contaminants

independently of their frequency of detection would give an unrealistic estimation.

It should be noted that shellfish other than soft-shell clams were harvested for analysis in the area studied, namely, the blue mussel and Arctic wedge clam (*Mesodesma arctatum*). Our results (data not shown) revealed that the concentrations of inorganic arsenic and PCBs in soft-shell clams were lower than those found in blue mussels and equivalent to those found in the Arctic wedge clam. Therefore, depending on the type of shellfish consumed, the cancer risk could be greater than or equivalent to the risks found in the present study.

The health effects were evaluated separately for each of the contaminants and not for the mixture of contaminants found in the shellfish. It is particularly interesting to note that the two contaminants that were independently associated with an excessive cancer risk have complementary modes of action. The precise mode of action involved in arsenic-induced cancer has not been established with confidence, but studies suggest that arsenic might act as a cocarcinogen, a promoter, or a progressor (NRC 2001). PCBs induce tumors primarily through modes of action that do not involve gene mutation (U.S. EPA 2003a). It is therefore possible that the cancer risks calculated here underestimate the actual risks of the mixture. However, our cancer evaluation could also overestimate the actual risks if neutral interactions exist. Also, it is possible that selenium found in shellfish could protect against the genotoxic effects of sodium arsenite (Biswas et al. 1999).

In the same way, absorption of contaminants combined with certain lifestyles may result in a marked increase in the cancer risk related to these contaminants. For example, the ingestion of water contaminated with inorganic arsenic combined with the inhalation of cigarette smoke gives the smokers a much higher risk of developing lung cancer than that predicted by an additive model for these two substances (Ferrecio et al. 2000; Tsuda et al. 1995).

Unfortunately, some important aspects limited the possible participation of shellfish harvesters in biomonitoring in the context of this study. First, the interviews carried out directly on the shore required a time-efficient procedure in order to maximize the participation rate, because the favorable period for shellfish harvesting is limited by sea tide. Second, a few of the sectors of study were considered closed areas by the Department of Fisheries and Oceans of Canada and, any operation involving personalized information collection would have been considered suspicious because the activity of shellfish harvesting was then illegal in such a case.

In general, we can assume that our risk evaluations are based on valid scenarios. Because the average shellfish consumption in

the United Kingdom (WHO 1985) varies from 13.0 to 18.9 g/day, our first scenario (17 g/day) appears to properly reflect the average consumer. The second scenario proposes a shellfish consumption equivalent to 40 g/day. This amount seems realistic because it is comparable with the 90th percentile of the amount consumed in the United Kingdom, evaluated at 36.4 g/day (WHO 1985). The scenario of a person whose daily shellfish consumption would be 56 g (the third scenario) is comparable with the daily seafood consumption of the residents of commercial fishing communities in the same region, 58.6 g/day (Dewailly et al. 1991). Finally, the value (95 g/day) for the fourth scenario is comparable with the value of 165 g/day recommended for characterizing the consumption of "maximum exposed individuals," or individuals who live mainly from the products of their fishing (Cooper et al. 1991).

These data have the undeniable quality of having been collected from shellfish harvesters and consumers. With an average shellfish consumption of 17 g/day/person, compared with an average of 3.81 g/day/person for the entire Canadian population (Statistics Canada 2002), the study population is a somewhat special population. However, comparison of the estimated values for each of the consumption scenarios with the values obtained for other populations leads to the conclusion that the consumption habits of the people surveyed are not exclusive to this population and could be observed in other populations.

## Conclusion

In the present study, none of the contaminants found in soft-shell clams could be associated with intakes that exceed exposure limit recommendations proposed to prevent non-cancer effects. However, several limits must be considered before drawing conclusions about the relative safety of shellfish consumption regarding this end point. Furthermore, cancer risks  $> 1 \times 10^{-6}$  were measured for inorganic arsenic and PCBs. Other studies are needed to better understand arsenic metabolism and the importance of the quantities absorbed based on the form ingested. Biologic sampling should also be considered for a few volunteer shellfish harvesters in a further study. Such biomonitoring would add the dimension of correlating levels found in people with those found in shellfish and with the fish consumption history of the subjects. Considering the results of the present study, the implementation of a program for monitoring the chemical contamination of recreational shellfish-harvesting areas is highly recommended; such a program could eventually lead to the production of a shellfish consumer guide.

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