Agricultural land application of municipal biosolids: PBDE and metal levels in cow's milk

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Abstract:

The impact of land application of biosolids (treated municipal sewage sludge) on dairy milk quality was measured in real farm operating conditions where biosolids were applied in accordance with the regulatory framework prescribed in the province of Quebec (Canada). The milk from 14 farms receiving biosolids were sampled in the Saguenay region in December 2009 and compared to the milk from 14 control farms. The tested farms had used biosolids an average of 11 years. Statistical analysis revealed no difference in the content of inorganic contaminants (arsenic, copper, molybdenum, zinc and thallium) in milk. These results suggest absence of induced hypocupriosis for dairy cows from farms using biosolids. However, the content of polybrominated diphenyl ethers (PBDEs) was higher in milk sampled from the farms using biosolids. Differences could be due, in part, by variability of exposition to dust among farm buildings. PBDE levels were however very low (mean value of 7,2 ng/L), and remained 3-7 times lower than the average levels recorded for various dairy products in the United States and

Europe (fat content basis). These low levels could be linked, in part, to lower air depositions on forage in the Saguenay region or lower dust contamination in farm buildings. Based on these results, current knowledge and available data, the application of municipal biosolids under Québec regulations would have no significant impact on PBDE exposure for consumers of dairy products produced in Quebec. The original version of this publication is titled « Épandage agricole des biosolides municipaux : contenu en métaux et en PBDE du lait de vache » and was published in VertigO - la revue électronique en sciences de l'environnement, Volume 11 Numéro 2 | 2011: http://vertigo.revues.org/

Résumé:

On a mesuré l'impact de l'épandage de biosolides (boues d'épuration municipales traitées) sur la qualité du lait de vache en conditions réelles d'opération à la ferme, selon le cadre réglementaire prescrit au Québec. Le lait de 14 fermes réceptrices de biosolides a été échantillonné dans la région de Saguenay en décembre 2009 et comparé au lait de 14 fermes témoin. Les fermes réceptrices avaient un historique moyen de 11 années d'épandage. L'analyse statistique révèle l'absence d'impact sur la teneur du lait en contaminants inorganiques (arsenic, cuivre, molybdène, zinc et thallium) et suggère l'absence d'hypocuprémie induite chez les bovins des fermes réceptrices. La teneur en diphényls éther polybromés (PBDE) était par contre plus élevée dans le lait du groupe de fermes avec biosolides. Cette différence pourrait être en partie attribuable à la variabilité de l'exposition aux poussières entre les bâtiments d'élevage. La teneur moyenne en PBDE du lait des fermes réceptrices demeure cependant très faible (7,2 ng/L), soit de 3 à 7 fois inférieure aux teneurs moyennes relevées pour divers produits laitiers aux États-Unis et en Europe sur base de la matière grasse. Ces plus faibles teneurs pourraient en partie être expliquées par des dépôts atmosphériques moindres sur les herbages au Saguenay ou par un niveau de contamination moindre des poussières de bâtiments d'élevage. Selon les résultats de cette étude, les connaissances actuelles et les données disponibles, l'épandage de biosolides municipaux selon le cadre réglementaire québécois serait sans impact notable sur l'exposition globale aux PBDE des consommateurs de produits laitiers du Québec. Cette publication est une traduction de l'article « Épandage agricole des biosolides municipaux : contenu en métaux et en PBDE du lait de vache » publié dans VertigO - la revue électronique en sciences de l'environnement, Volume 11 Numéro 2 | 2011: http://vertigo.revues.org/

Key-words: Biosolids, copper, cow's milk, flame retardants, metals, molybdenum, PBDE, sludge, thallium.

Introduction

The 700-odd municipal wastewater treatment facilities in Québec produce around 900 000 tonnes of municipal sludge per year on a wet basis (Hébert et al., 2008). That sludge is the by-product of an assortment of processes to reduce the presence of pathogenic microorganisms and extract nutrients and organic matter that would promote eutrophication if discharged into lakes and rivers. For terrestrial environments, the extracted components have useful properties, since both the organic matter and mineral elements like phosphorus and nitrogen can increase soil fertility and improve plant productivity (Beecher, 2009; Perron and Hébert, 2008; BUC, 2008). But before such sludge can be applied to the land it must meet quality criteria, particularly in terms of disinfection and levels of metals, dioxins and furans (MDDEP, 2008). Spreading it on farmland must also be done in accordance with regulatory standards and criteria in force (MDDEP, 2008). Both conditions were met in the municipal biosolids referred to here.

Each year, municipal biosolids are applied to less than 0.5 % of the farmland in Québec (Hébert et al., 2008). For the minority of farmers involved in this activity, there is less need to purchase mineral fertilizers (BUC, 2008). At a time when phosphorus deposits are increasingly rare worldwide (Soil Association, 2010), increased recycling of biosolids would reduce Québec's dependence on imported mineral fertilizers. For municipalities, this solution to sludge management produces less greenhouse gas emissions than disposal by incineration or in technical landfills (Sylvis, 2009).

At present in Québec, only 27 % of the sludge produced is applied to farmland, versus 70 % and 90% in France and Norway respectively (Hébert 2010). By 2015 the Government of Québec intends to raise that proportion considerably, the target being to recycle onto soils 60 % of all organic matter, including municipal sludge, with or without composting or prior methanation (MDDEP, 2011). In the Saguenay region this objective has already been met for municipal biosolids, which have been applied to farmland there for over 20 years (Figure 1). Indeed, since 1994, 100 % of Saguenay's municipal biosolids have been recycled using land application and composting.

Figure 1: Recovery of biosolids stored in the field for spreading on a farm in Saguenay. (Photo: Guy Gagnon)

Because sewage sludge retains some of the metals and chemical contaminants in raw municipal wastewater, the recycling of it on farmland has raised many concerns (Harrison and McBride, 2009; Desmarais, 2006; McBride, 2003). In the last 30 years, numerous studies have been conducted in various countries to document contaminant levels in sludge and the potential risks of applying it to the land. That research has in turn given rise to a number of synthesis studies (WEAO, 2010; Pepper and Zerzghi 2008; MDDEP, 2006; NAS, 2002; WEAO, 2001). Generally, these syntheses indicate that risk levels are relatively low by the standards in force in the countries concerned, but that further studies are needed, particularly with regard to emerging contaminants of concern (ECCs) (Hydromantis, 2010; 2009). Among the ECCs are a wide range of compounds found in common consumer products, such as pharmaceuticals and personal care products. Such compounds tend to pass into human excrement and domestic greywater, and thus into the sludge at treatment facilities (Xia et al., 2010). Many ECCs are strongly degraded by sludge treatment (Hydromantis, 2010) or are metabolized in the aerobic conditions on the soil after biosolids are applied to farmland. This is the case particularly with hormones and nonylphenols (Andrade et al., 2010; Whalen and Hébert, 2010; Xia et al., 2010), and the antibacterials triclosan and triclocarban (Xia et al., 2010).

The potential risks that are of greatest concern involve molecules with the following characteristics: high toxicity, high levels and persistence in treated sludge, persistence in receiving soils and bioaccumulation in the food chain (BNQ, 2009). Contaminants combining at least two of these characteristics include certain Inorganic trace elements (ITE), such as cadmium (Cd), copper (Cu), mercury (Hg), zinc (Zn) and lead (Pb), and organic compounds like dioxins and furans (PCDD/PCDF), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), which are flame retardants.

A recent study indicates that levels of several metals in Canadian municipal sludge have declined considerably, particularly Cd, Hg and Pb (Hydromantis, 2010). This corroborates an earlier Québec study showing that sludge from municipal facilities now contains, on average, no more metals than sludge from septic tanks at isolated residences where there is no industrial input (Perron and Hébert, 2007b). However, levels of some metals like Cu and Zn are still higher in biosolids than in natural soils (Perron and Hébert, 2007b). Repeated application of biosolids could therefore, over time, lead to the receiving soils becoming enriched in these metals, as has been demonstrated in long-term experimental parcels in the United States (Pepper and Zerzghi, 2008).

Perron and Hébert (2008) have determined the enrichment in several ITEs of Saguenay farmland that received 4 to 12 applications of biosolids per field, in real conditions and in accordance with regulations. For the metals studied, soil quality was not altered by these repeated applications, either in terms of the criteria for metallic cations developed by the Institut de recherche et de développement en agroenvironnement (Giroux et al., 2008), or in terms of the criteria for Hg levels developed by the CCME (2007). There was however significant enrichment in bioavailable Cu and Zn (Mehlich 3). In the medium term, the increase in soils of bioavailable Cu and Zn could result in higher levels of Cu and Zn in forage crops, both being essential elements for livestock. But if biosolids are applied repeatedly on the same parcels over decades, there could be a risk of exceeding soil criteria (Perron and Hébert, 2008).

The Saguenay study did not document soil enrichment in ITEs of the anionic type, such as arsenic (As), molybdenum (Mo) and selenium (Se), due to the limitations of the experimental design. However, Mo in soil accumulates readily in various plant parts (Chaney, 1990). While such bioaccumulation is not necessarily problematic for plants, it has been shown that lowering the Cu/Mo ratio in livestock feed can induce a copper deficiency that is detrimental to the health of cows (Ward, 1978). Based on studies done in experimental parcels in New England, Harrisson and McBride (2009) have suggested that biosolids application could affect livestock health, not only through bioaccumulation in pasture crops but through the accidental ingestion while grazing of particles of soil and biosolids. Since greater Mo input in cow feed translates directly into much higher Mo levels in milk (Ward, 1978), a very high level of Mo in milk from farms receiving biosolids would indicate a risk of copper deficiency in the cows. Also not documented by the Saguenay study (Perron and Hébert, 2008) was soil enrichment in thallium (Tl), another ITE that is a subject of concern relative to recycling biosolids on farmland (WEAO, 2010; McBride, 2003).

Among the organic contaminants in biosolids that combine toxicity, persistence and bioaccumulability, dioxins and furans have been monitored for a number of years in Québec (MDDEP, 2008). Their levels are declining, and now generally are at very low levels in municipal biosolids (Hydromantis, 2010; Groeneveld and Hébert, 2004). This is also the case with PAHs (Hydromantis, 2010; Groeneveld and Hébert, 2004) and PCBs (MDDEP, 2008; Groeneveld and Hébert, 2004). These low levels are primarily the result of effluent discharge standards aimed at reducing contamination at the source, as well as the banning of various commercial products (Hydromantis, 2010). On the other hand, levels of polybrominated diphenyl ethers (PBDEs) are still relatively high in municipal sludge (WEAO, 2010; Harrisson and McBride, 2008).

PBDEs are synthetic flame retardants added by manufacturers to plastic matrices, synthetic resins and textile fibres to reduce the flammability of a host of products, thereby reducing fire risks in the home and workplace. Many products are therefore likely to contain PBDEs: the padding material in furniture, the cases of electrical appliances (televisions, computers, etc.), automobile parts, plastic pipes, plastic-based building materials, electrical wires, circuit boards, adhesives, sealants, toys and tissues, etc. (Berryman et al., 2009; Alaee et al., 2003). Since all of these objects degrade over time, they are a source of dust that may be inhaled or ingested in homes and other buildings (Schecter et al., 2006).

PBDEs are toxic substances within the meaning of the Canadian Environmental Protection Act (Berryman et al., 2009). They are hormone disruptors, interfering with the animal endocrine system (Mariussen and Fonnum, 2003). An epidemiological study found a relation between high exposure to PBDEs and neurological effects on children (Herbstman et al., 2010). Dust is now considered the principal source of PBDE exposure in humans (Johnson et al., 2010; Jones-Otazo et al., 2005). PBDEs are also found in food products, primarily those of animal origin (Schecter et al., 2006; Bocio et al., 2003). Part of the inhaled or ingested PBDEs is subsequently excreted into wastewater through toilets; the dust is also discharged into sewers in domestic greywater. PBDEs thus end up in wastewater treatment facilities where, because they adhere strongly to organic matter and are relatively unaffected by treatment processes (WEAO, 2010), for the most part they are concentrated in biosolids (Smyth et al., 2009).

With structural characteristics similar to those of PCBs, PBDEs are persistent in the soil, their half-life ranging from 10 to over 20 years depending on congener (Andrade et al., 2010). American studies that followed more than 20 and 30 years of repeated biosolids application indicate that most of the PBDEs would indeed have persisted in the soil (Xia et al., 2010; Pepper and Zerzghi, 2008). This is why PBDEs, among all the emerging organic contaminants in municipal sludge, are of special concern (Hydromantis, 2010; Harrisson and McBride, 2009).

Like other halogenated compounds with a high molecular weight, such as PCBs and dioxins and furans, PBDEs that have accumulated in receiving soils are poorly absorbed by plant roots (Xia et al., 2010). For example, no PBDEs were detected in corn cultivated on soil that was intensively fertilized with biosolids for 33 years (Xia et al., 2010). Nonetheless, certain authors (Kierkegaard et al., 2009; Harrisson and McBride, 2009) have suggested that there could be an impact on PBDE levels in cow's milk, specifically through the involuntary ingestion of soil and biosolids in pastures fertilized with biosolids. We could not find any study in the literature that confirmed this hypothesis. Moreover, contrary to American and most European standards, Québec prohibits the application of biosolids on pastures. There is an exception for certain biosolids certified by the Bureau de normalisation du Québec (MDDEP, 2008), but in practice they are mostly used on grain crops. However, land that has received biosolids may be returned to pasturage after one year, so cattle could ingest soil enriched in PBDEs, since the biosolid particles would be mostly fragmented and incorporated into the soil by earthworms and other detritivores.

In this context, the present study sought to determine whether the accumulation of Cu and Zn observed in Saguenay agricultural soils has an influence on milk quality. We compared the milk from farms that receive biosolids to the milk from control farms that do not receive biosolids, in real operating conditions instead of on experimental parcels. We included an exploratory component that documented levels of anionic ITEs (As and Mo) for which soil enrichment could not be quantified in the earlier study, and levels of persistent ECCs like Tl and PBDEs. Where applicable, the results were compared to various standards, criteria or reference data so we could estimate the potential impact on the health of consumers.

Materials and Methods

Selection of sampling sites

The territory of Ville de Saguenay was chosen as the sampling site because it pioneered biosolids recycling in Québec and has a complete record of land applications going back to 1991 (Perron and Hébert, 2008).

Of the thirty farms listed in the register, we chose the 14 dairy farms that had made the most frequent use of biosolids since 1991. The control group was chosen from a list of 20 dairy farms in the same area provided by regional stakeholders. The control farms were known to have never applied municipal biosolids or pig slurry on their land (pig slurry is rich in Cu and Zn). The final selection of 14 control farms was guided by a search for average characteristics comparable to those of the 14 farms "with biosolids", regarding herd size, animal type, whether or not the animals were put out to pasture, and whether or not rubber mats were used in the cowshed (Table 1).

These criteria were chosen primarily to limit the variability of potential sources of PBDEs. Being strongly hydrophobic, PBDEs are retained by the fat in animal products (Schecter et al., 2006). But the fat content of milk depends in part on which breed of cow produces it. Similarly, mats of recycled rubber in cowsheds could contain PBDEs and also end up in the milk.

Two other important variables could not be controlled nor measured, due to limitations of the experimental design. These were: dust contamination in cowsheds, and atmospheric deposition of PBDEs that adhere to the foliage of forage crops (Xia et al., 2010; Kierkegaard et al., 2009; Moon et al. 2006; Lee et al., 2004). Together with grains, such crops constitute most of the feed of Saguenay dairy cows.

Selection of parameters to analyze

Since there is significant enrichment of bioavailable Cu and Zn in receiving soils (Perron and Hébert, 2008), both of these ITEs were chosen for the milk analysis. We also chose to analyze for Mo, As and Tl for exploratory purposes. Selenium was not chosen because this micronutrient is often present in mineral supplements added to cow rations. Table 2 shows the levels in Saguenay biosolids for the ITEs considered in the present study.

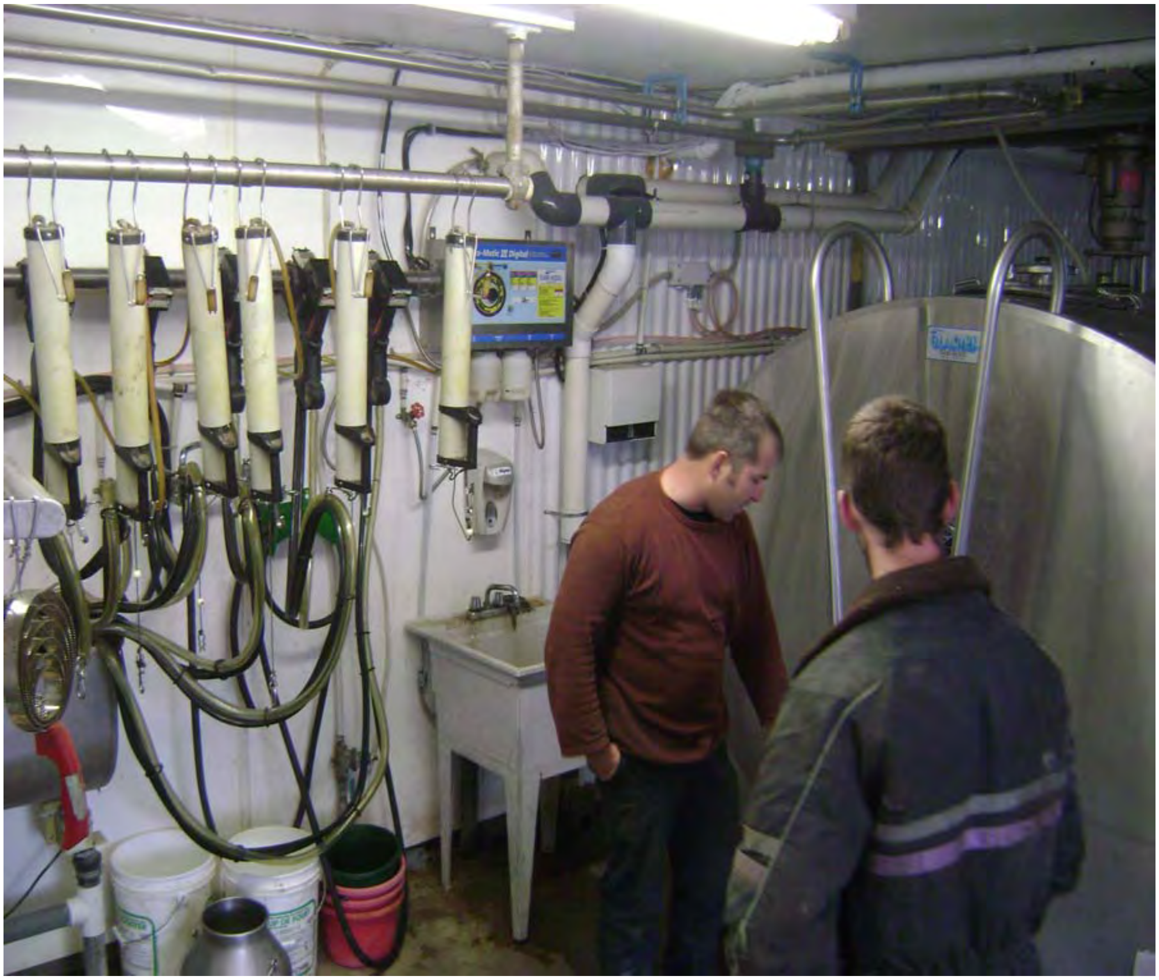
PBDE molecules have one to ten atoms of bromine; there are therefore many congeners, some more toxic than others. To simplify the data analysis on milk quality and obtain a better risk estimator, we chose the summation of congeners 47, 99, 100, 153 and 154 (∑ congeners 47, 99, 100, 153, 154), following the example of a major American study on PBDE levels in receiving soils (Xia et al., 2010). Besides being the most abundant congeners in biological samples, food and milk, they also carry the greatest risk (Kierkegaard et al., 2009; Schecter et al., 2006; Bocio et al., 2003; Mariussen and Fonnum, 2003). The PBDE levels in Saguenay biosolids are shown in Table 3. Also presented by way of indication is the parameter for total PBDE (∑ Total) which combines all of the congeners including BDE-209, or deca-BDE. In view of the lipophilic nature of PBDEs, we also analyzed the milk's fat content.

Milk sampling

Two series of milk samplings were conducted over 2 separate weeks in December 2009, with 14 samples of milk per series, to obtain a proportional representation of both groups of farms in each series. For comparison, we also added 4 samples of commercial milk containing 3.25 % fat. Two of the latter were from regional dairies in Saguenay, while the other two were purchased in the Laval and Québec areas. We did not do repeat sampling over time because of the high cost of PBDE analysis.

Sample collection at the farm was done from the producer's milk tank (Figure 2), using equipment that would not contaminate samples for the parameters studied. A one-litre glass jar was used to collect approximately 600 ml of farm milk. The jar was handled using a clamping collar, snap-hook and rod, all of stainless steel like the milk tanks and components. To ensure homogeneity, before sampling the milk was mixed for five minutes in the tank, as is standard practice for milk fat analysis. Fifty ml of the sample was then poured into a plastic container for fat analysis. The rest of the sample was poured into a one-litre amber glass jar supplied by the Centre d'expertise en analyse environnementale du Québec (CEAEQ). A backup sample was also taken. Before and after each sampling the equipment was rinsed with distilled water to avoid cross contamination. The commercial milk was sampled in a similar manner, directly from the milk cartons. We also sampled biosolids from the 2 principal treatment facilities in Saguenay (Chicoutimi and Jonquière) for PBDE analysis. All samples were kept cold and transported to the laboratories within 48 hours.

Figure 2: View of the milk room of one of the 28 participating farms. At left is the milking equipment, at right the refrigerated milk tank.
(Photo: Dominic Lemyre-Charest)



Laboratory analyses

Fat analysis of the farm milk was performed by Valacta inc. using the infrared method, following the procedure used for the Fédération des producteurs de lait du Québec (Federation of Québec milk producers). All other analyses were performed by the CEAEQ in Laval. For the commercial milk, which was 3.25 % M.F. milk homogenized at the dairy plant, chemical analysis was preferred. The samples went through the extraction steps within 5 days of collection at the farm, without having been frozen except in certain cases. Extraction for ITEs was done using current methods (CEAEQ, 2010) by hydrochloric acid and nitric acid digestion at 95 °C for two hours. The analysis was done using inductively coupled plasma mass spectrometry (ICP-MS).

The extraction and analysis of PBDEs turned out to be complex and required tweaking by CEAEQ chemists over the course of the project. Given the limited capacity of the extraction equipment, each of the two series of fresh milk samples was subdivided into 2 sub-groups, and the 4 sub-groups were extracted at different times. The extractions from series 2 (the third and fourth sub-groups) had to be repeated using frozen samples to meet the CEAEQ's quality control criteria. Frozen milk has been used by other authors such as Kierkegaard et al. (2009), and is not supposed to alter the results.

The extraction process was based on the AOAC method (1992). A 100 ml sample of milk was first fortified with an isotopic solution of PBDEs marked with ^{13}C, for the purpose of later quality controls. The fortified sample was then extracted in the flask with a mixture of ethyl alcohol, ammonium hydroxide and hexane. The hexane fraction was then recovered, while the residual fraction was extracted twice again, with a mixture of ethyl alcohol and hexane. The hexane from all 3 extractions was then recovered, dried using anhydrous sodium sulfate, then evaporated to a volume of 6 ml. This extract was then treated with sulfuric acid to eliminate the lipids, then purified using an initial multilayer column (silica, acidic silica, basic silica and silica impregnated with silver nitrate) followed by a second column of alumina (50 g). Such columns allow the removal, by reaction and selective adsorption, of most of the organic compounds co-extracted with the PBDEs. The acid digestion and purification followed an analytical protocol for analyzing PCBs in biological matrices (CEAEQ, 2006). The purified extract was then concentrated by evaporation and transferred into a vial. A volumetric standard was added to make a final volume of 500 µl. The final extract was kept cold until its injection into a gas chromatograph coupled to a high-resolution mass spectrometer.

The raw PBDE levels obtained were corrected based on the recovery rate of standards marked with ^{13}C. The recovery percentages met quality control criteria, except for congener PBDE-209 (decabromodiphenyl ether), which often presents analytical difficulties with these matrices (Frederiksen et al., 2008; Kierkegaard, 2007), but this congener was not included in the milk study. For each sub-group of milk samples, a laboratory blank was introduced during extraction to control for ambient contamination in the laboratory by dust or reagents. Ambient levels in the blank were subsequently subtracted from the values obtained for the samples. Based on CEAEQ criteria, a final value below the detection limit was considered "not detected" (ND), while a positive value less than 3 times the detection limit was considered "detected but not quantified" (DNQ).

Statistical analysis

For fat content, means from the 2 groups of farms were compared using a Student's t-test. Since the distributions of values for As, Cu and Mo did not meet the hypothesis for normality in a satisfactory manner, we used the Wilcoxon/Kruskal-Wallis test by ordination for all ITEs, assigning to ND values half the detection limit. We also preferred to present median values instead of means, since all Tl values were below the detection threshold, as were most (75 %) of the data for As. When the median corresponded to an ND value, we indicated the detection threshold in the results table. The statistical software used for these tests was JMP version 8.1a. No test was run for Tl, since all values were below the detection threshold.

For PBDEs, we calculated both the median and the mean, assigning the detection limit to DNQ values and half the detection limit to ND values. A Student's t-test was performed for the comparison of means, after first normalizing the data by a logarithmic transformation (ln x) due to the high variability of levels. This test was run using SigmaStat version 3.1.

Results and discussion

Representativeness arms and biosolids

The 2 groups of dairy farms were broadly comparable in terms of breed and herd size (Table 1). The control group did have a higher proportion of farms where the cows were pastured and/or where rubber mats were used in the cowshed. However, the principal difference concerns the use of biosolids. Farms that received biosolids had done so for an average of almost 11 years, the maximum being 18 years for farm z2, which has participated in Saguenay's biosolids application program since 1991. Where biosolids are concerned, these farms are probably the most exposed sub-population of dairy farms in Québec.

Table 1: Description of the groups of dairy farms studied.

	Farms with biosolids	Control farms
Number of farms	n=14	n=14
Breed of cows	Holstein	Holstein
Mean number of lactating cows	x = 51 (22 to 70)	x = 48 (28 to 70)
Farms using pasturage	36 %	64 % (50 %)[1]
Cowsheds with rubber mats	50 %	86 %
Number of years with biosolids applications	x = 10.7 years (4 to 18)	0

[1]: Leaving out 2 farms that made very little use of pasturage, the result is 50 %.

As can be seen below, ITE levels in Saguenay biosolids are analogous to the Québec means for As, Mo and Zn (Table 2). The lower Cu levels in Saguenay biosolids could be explained by the fact that the drinking water is less highly chlorinated and therefore less corrosive to domestic copper piping. Tl was not detected (< 0.1 mg/kg).

Table 2: Mean levels of several ITEs in different municipal biosolids (mg/kg dry basis).

Origin of biosolids	As	Cu	Mo	Zn	Tl	Sources
Ville de Saguenay	3.0	194	4.1	239	< .1	Perron and Hébert (2008), except Tl: unpublished data. Means for 6 samples.
Province of Québec – automated facilities	3.8	402	5.4	398	-	Perron and Hébert (2007b). Means for 35 treatment facilities.

The total PBDE level in Saguenay biosolids is significantly lower than the medians for Canada and the United States (Table 3). However, the median level of 1040 ug/kg in Saguenay sludge is similar to that of a Canadian sludge produced by a similar process (Environment Canada, unpublished data). The summation figures for congeners 47, 99, 100, 153 and 154 follow the same trend.

Table 3: Median levels of several PBDEs in different municipal biosolids (ng/g or ug/kg, dry basis).

	∑ Total	∑ congeners 47, 99, 100, 153, 154	%	Source
Saguenay (n=2)	1040	397	38 %	Present study
Canada (n=9)	2520	866	34 %	Environment Canada (unpublished data)
United States (n=74)	2590	1366	53 %	USEPA (2009), adapted from WEAO (2010)

Levels of fat and dry matter in milk

Milk from the 2 groups of farms turned out to be identical in terms of fat and dry matter levels (Table 4). This suggests that the 2 groups are similar with regard to the main parameters of dairy production. It also implies that when interpreting the PBDE analyses there is no need to normalize fat levels in the milk from the farms.

Table 4: Mean levels of fat and dry matter in milk from the farms, by group.

	Fat (%)	Dry matter (%)
Farms with biosolids (n=14)	3.98	12.7
Control farms (n=14)	3.94	12.6
Result of statistical analysis	$p = 0.60$ n.s.	-

Levels of inorganic trace elements in milk

Table 5 presents the median levels of ITEs in milk from the 2 groups of farms, with the results of the statistical analysis. For As, the median levels are identical and below the detection threshold (< 0.0002 mg/L). The highest values measured are actually 28 times lower than the Québec standard of 0.025 mg/L for drinking water (Table 5), indicating that there is no risk to consumers.

Table 5: Levels of inorganic trace elements in farm milk (mg/L).

		As	Cu	Mo	Tl	Zn
Farms with biosolids (n=14)	Median Min Max	< 0.0002 < 0.0002 0.0017	0.064 0.044 0.16	0.036 0.031 0.043	< 0.01	3.1 2.7 3.3
Control farms (n=14)	Median Min Max	< 0.0002 < 0.0002 0.0009	0.075 0.031 0.15	0.038 0.031 0.051	< 0.01	3.1 2.8 3.6
Statistical tests [1]	*P value*	0.51	0.57	0.38	-	0.50
Commercial milk (n=4)	Median	< 0.0002	0.069	0.042	< 0.01	2.95
Québec standard for drinking water		0.025	1.0	-	-	-

[1]: For the statistical treatment of data, see the Materials and Methods section.

Copper was detected in all of the milk samples. Contrary to what was expected, the median was slightly lower for the group with biosolids, though the difference was not statistically significant (Table 5). This result is surprising, since it is known that farm parcels that receive biosolids are enriched in bioavailable Cu (Perron and Hébert, 2008). Nonetheless, the highest Cu levels found are 6 times lower than the Québec standard for drinking water. The absence of impact for the farms receiving biosolids could be explained by the fact that soil levels of Cu have less effect on plant absorption than do other factors like soil pH and plant species (Basta et al., 2005). As well, only some parts of the fields received biosolids, since the dairy farms spread their own manure first.

Zinc levels in the milk are also identical between the 2 groups of farms. As with Cu, higher Zn levels in the soil (Perron and Hébert, 2008) have had no effect on milk quality. Nor was there any impact on Mo levels. Since there is a direct relation between Mo levels in cattle feed and in the milk they produce (Ward, 1978), we may deduce that biosolids use caused no increase in Mo levels in cattle feed on these farms, and that contrary to the hypothesis of Harrisson and McBride (2009) it has not led to a risk of hypocuprosis. We must however specify that, unlike the United States federal regulations, Québec limits Mo levels in biosolids. Biosolids produced in Québec have average Mo levels comparable to those of pig slurry and poultry manure (Perron and Hébert, 2007b). As well, the determining factor in plant absorption of Mo is soil pH, rather than the level of total Mo present.

As for thallium, it was never detected in any of the milk samples, despite a very sensitive analytical threshold (0.01 mg/L). According to certain authors (Tremel-Shaub, 1997), cattle can ingest plant crops containing up to 1 mg/kg DM of Tl without any problem. That is a far higher level than is found in Saguenay biosolids (< 0.1 mg/kg) and Canadian sludge (0.26 mg/kg). Tl levels in Canadian sludge have declined some 60 times over in recent decades, thanks to industrial clean-up operations (WEAO, 2010). Levels in Canadian biosolids are actually below the levels of 0.5 to 1.5 mg/kg found in natural clay soils (Kabata-Pendias, 2000). Input from biosolids is therefore unlikely to enrich soils significantly in Tl, a conclusion indirectly corroborated in the case of Saguenay by the non-detection of Tl in farm milk.

Overall, the results indicate that for a group of dairy farms that are among the most exposed to municipal biosolids in Québec (with an average 11 seasons of application), and in the context of Québec regulations, the levels in milk of As, Cu, Mo, Tl and Zn have not been altered by biosolids application and are negligible relative to drinking water quality standards (for As and Cu). And this is despite the fact that repeated application has caused significant soil enrichment in certain ITEs (Cu and Zn). Consequently, there is little probability that continued applications on the same farms would have a longer-term impact on milk quality. This invalidates the hypothesis that milk from farms using biosolids would be higher in micronutrients (Cu and Zn). Nevertheless, as a preventive measure aimed at protecting crops, the Government of Québec (MDDEP, 2010) has placed restrictions on the application of biosolids on soils already strongly enriched in Cu by inputs such as slurry from nursery and maternity hog operations. The latter do in fact contain higher levels of Cu and Zn than municipal biosolids (Perron and Hébert, 2007b).

From these results it can be deduced that for other ITEs like Cd and Pb, whose presence in Saguenay sludge is now on the order of the "background noise" of natural soils (Perron and Hébert, 2007b; 2008) the impact on milk quality of applying municipal biosolids is probably low or negligible. The results could also be transposable to other parts of Québec where biosolids are applied repeatedly under similar farm conditions. With the exception of Cu, most Québec biosolids have ITE levels analogous to those in Saguenay (Perron and Hébert, 2008) and application practices throughout the province are subject to the same restrictions, especially in terms of phosphorus load (MDDEP, 2008). The situation may be different in the United States, where much higher quantities of sludge can be applied because doses tend to be based on nitrogen needs rather than phosphorus. As well, so far American federal regulations do not restrict Mo levels in biosolids.

PBDE levels in milk

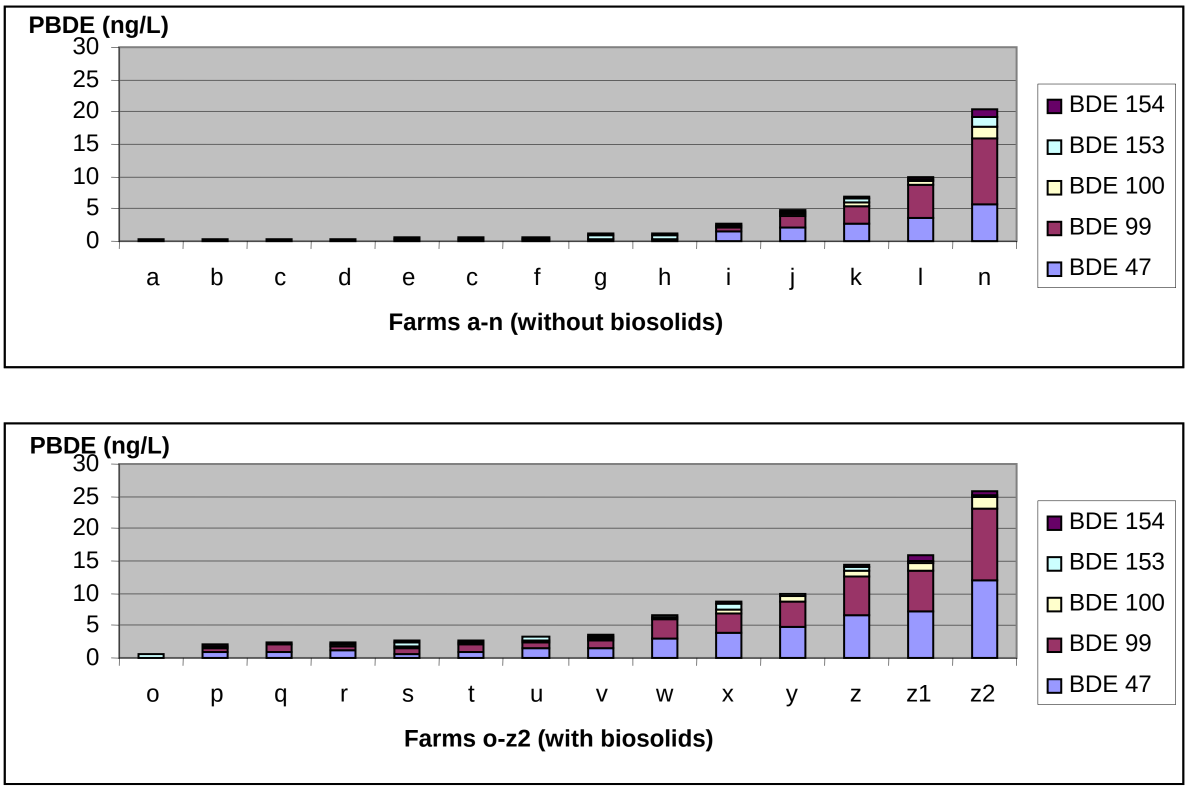
PBDEs were detected in half the samples from the control farms and most (13/14) of the samples from farms using biosolids. The levels measured are often close to the quantification threshold and on the order of a ng/L (one millionth of a ppm), which goes to show the great sensitivity of the laboratory equipment. As can be seen from Table 6, the mean PBDE level in the milk from farms with biosolids is statistically higher than the control farms. This might seem to suggest that the difference between the 2 groups can be attributed to the application of biosolids. Indeed, the milk from farm z2, which received biosolids the most frequently (18 seasons of applications), contained the highest level of PBDEs (Figure 3). But the exact origin of the PBDEs found is hard to determine. For example, no PBDEs were detected in milk from the farm that had received biosolids for 17 years. And the milk from farm n, which had never received biosolids, contained the second highest level of PBDEs of all 28 farms.

Table 6: PBDE levels (∑ congeners 47, 99, 100, 153, 154) in cow's milk (ng/L or pg/ml).

	Farms with biosolids (n=14)	Control farms (n=14)	Results of statistical tests (values of p)
Mean	**7.2**	**3.6**	**0.01**[1]
Median	**3.5**	**0.9**	
Min	**0.6**	**0.3**	
Max	**25.8**	**20.5**	

[1]: The means are significantly different

Figure 3: Levels of several PBDE congeners in milk (ng/L) from farms without biosolids (Figure 3a) and farms with biosolids (Figure 3b).



One explanation that can be excluded right away is plant absorption of PBDEs from the soil, which is considered negligible (Xia et al., 2010). Soil ingestion in the pasture is a more likely source (Harrisson and McBride, 2009), but of the 5 farms with biosolids whose milk had the highest levels of PBDEs, only one pastured its cows. Furthermore, the 5 control farms with the highest levels of PBDEs did not pasture their cows. This suggests that pasturing is not a dominant exposure pathway for PBDEs, either in the present study or elsewhere in Québec. For one thing, the application of municipal biosolids to pastures is prohibited in Québec; for another, receiving soils are rarely returned to pasturage even after the mandatory one-year wait, since in practice they tend to be located far from livestock buildings.

The control group had a higher proportion of farms using rubber mats (Table 1). Such mats appear to be a very limited source of contamination, since 6 of the 7 control farms with rubber mats had PBDE levels below 0.6 ng/L. It seems more likely that in the mechanically harvested hay and forage at certain farms there were particles of dry biosolids picked up from the surface of the soil by harvesting equipment. That however does not explain the high results for farm n and a few other farms that did not receive biosolids (Figure 3a). There is considerable variability among farms in the control group, the highest value being 20 times higher (2000 %) than the lowest value.

There were also other major sources of variation that could not be controlled by the experimental design, including atmospheric deposition on harvested forage. Kierkegaard et al. (2009) concluded that atmospheric deposition on forage was the principal source of contamination in milk from a farm in the United Kingdom, based on mass balance and the similarity of the PBDE "signature" in the milk, forage and atmospheric precipitate samples. The authors did not measure exposure to dust however. Plus, the PBDE levels they measured were 7 times higher than in the present study, for the same congeners.

A comparison of PBDE levels in Saguenay milk with other data in the literature sheds further light on the matter. When all values are expressed on a fat basis (Table 7), the PBDE levels in milk from Saguenay farms with biosolids are proportionally 3 to 7 times lower than the means reported for dairy products in the United Kingdom (Kierkegaard et al., 2009), Catalonia (Bocio et al., 2003) and the United States (Schecter et al., 2006). Yet the United Kingdom study did not involve biosolids. As for the American values, they could not have been influenced to any substantial degree by biosolids application since the latter concerns less than 1 % of American farmland annually (Beecher, 2009). This seems to confirm the possible importance of atmospheric deposition.

Table 7: Mean PBDE levels in different milks and dairy products, in ascending order, expressed on a fat content basis (∑ congeners 47, 99, 100, 153, 154).

		∑ PBDE ng/kg (fat basis)
Commercial - Province of Québec	n=4	106
Milk from farms with biosolids - Saguenay	n=14	180
Dairy products - Spain	n=4	495[1]
Dairy products - U.S.[2]	n=15	699
Farm milk - United Kingdom[3]	n=1	1203
Maternal milk (U.S.)[2]	n=62	66 000[4]

[1]: Bocio et al. (2003). The authors assigned a value of zero to non-detected analytes.
[2]: Adapted from Schecter et al. (2006).
[3]: Adapted from Kierkegaard et al. (2009).
[4]: Summation of all PBDE congeners, including BDE 209.

Shen et al. (2006) report PBDE levels in air that vary by a factor of 10 depending on region, while Frederiksen et al. (2009) report that atmospheric deposition of PBDEs tends to be lower at northern latitudes. Unlike southern Québec, the Saguenay region could be less affected by air from urban areas (Pierre Walsh, pers. comm.). The lower levels of PBDEs measured in Saguenay milk, regardless of whether the farms used biosolids, could therefore reflect lower atmospheric deposition of PBDEs.

However, within a given region atmospheric deposition should be more uniform, so this factor cannot explain the great variability among farms in the present study. Another source of variation could be adsorption of PBDEs on the lipophilic leaf cuticle of forage crops. It could be selective, as is the case with PCB adsorption on conifer needles, which varies by species and specific surface (Walsh, 2011). The dynamic of PBDE adsorption and desorption on foliage also seems to vary in time depending on the weather (Walsh, pers. comm.). Atmospheric conditions before the harvest, varying from farm to farm, could therefore influence PBDE levels in hay and forage. There could also be significant sources of PBDE emissions at the local level, such as illicit burning of waste containing PBDEs (Shen et al., 2006).
Airborne dust in livestock buildings could be a better explanation of the variability of PBDE levels within the 2 groups of farms. Indeed, airborne dust is now recognized as the principal source of contamination in humans, with food coming second (Johnson et al., 2010; Frederiksen et al., 2008). Like humans, dairy cows spend most of their lives in buildings containing dust. Since cows feed on hay and other plant products that are less contaminated than much of the food consumed by humans, it could be that dust is an exposure pathway of proportionally greater importance for cattle. The amount of dust and its PBDE levels could be highly variable from one farm to another, much as dust levels vary between different homes (Johnson et al., 2010). Rudel et al. (2003, cited by Xia et al., 2010) report dust in some homes with maximum values 100 times greater than the median.

The importance of the exposure of livestock to dust in farm buildings would be consistent with the fact that PBDE levels in bacon sold in the United States can vary by a factor of 100 (Schecter et al., 2006). Unlike dairy cows, hogs are rarely exposed to forage crops because they are essentially fed on grains, which are low in PBDEs. The great variability in dust exposure between different farms could therefore explain why no PBDEs were detected on several farms without biosolids, while other farms had PBDE levels twenty times higher than half the detection limit (Figure 3). This would then be a major co-variable that could not be controlled by the experimental design. A non-uniform distribution of this highly variable parameter between the 2 groups of farms could explain a good part of the difference observed, although forage contamination by biosolid particles on some farms but not others cannot be completely excluded.

Having attempted to explain the origin of the PBDEs in Saguenay farm milk, it is pertinent to consider the potential impact of these levels on the health of consumers. In adults, Schecter et al. (2006) have calculated that dairy products contribute less than 15 % of all PBDEs from food. Food inputs are themselves responsible for only part of the body burden of PBDEs in humans, most of it coming from the inhalation of air and dust in the home (Johnson et al., 2010; Schecter et al., 2006; Jones-Otazo et al., 2005). As well, the PBDE levels in milk from farms using Saguenay biosolids are much lower than those in dairy products elsewhere in the world (Table 7). That milk would therefore not contribute in any significant way to the body burden of PBDEs in adults who consume it.

Furthermore, if we assume that fewer than 1 % of Québec dairy farms use biosolids, and suppose conservatively that milk from the most biosolids-exposed farms would contain twice the PBDEs of other Saguenay milk products, it follows that biosolids application would contribute less than 2 % of the PBDE load in farm milk produced in Québec. Since 98 % of that load would come from farms that do not use biosolids, it is therefore primarily attributable to atmospheric deposition and dust. In reality, the proportion from biosolids is probably even lower, since most Québec dairy farms are located in the St. Lawrence Valley, where there is greater exposure to atmospheric deposition of PBDEs from the urbanized areas around the Great Lakes. Thus the agricultural recycling of biosolids, in accordance with Québec regulations, has a negligible impact on PBDE exposure among Québec adults.

Congeners 47 and 99, which represented 80 % of the PBDEs under study for both groups of farms, accumulate in the various parts of a cow according to the distribution of fat (Kierkegaard et al., 2009). One can deduce from this that levels in the meat of cows would be the same as in their milk, on a fat content basis. Thus, for the PBDEs under study, the meat of Saguenay dairy cattle would have average levels on the order of 180 ng PBDE/kg M.F, which is 4 times less than the average for the meat from cattle in the United States (Schecter et al., 2006).

The consumption by young children of milk or meat produced by Saguenay dairy farms, with or without the use of biosolids, probably has even less impact. This is because young children have greater exposure to house dust (Frederiksen et al., 2008) and nursing infants receive maternal milk containing an average of 66 000 ng/kg M.F. of PBDEs. That is 360 times more (36 000 %) than the milk from Saguenay farms with biosolids (Table 7).

The Government of Canada has instituted reduction-at-source measures aimed at the virtual elimination of tetraBDE, pentaBDE and hexaBDE congeners, which are considered the most bioaccumulable (Government of Canada, 2008). It has also announced its intention to tighten regulations on authorized PBDEs, by imposing usage restrictions on decaBDE (Berryman et al., 2009; Environment Canada and BSEF, 2009). As with the significant reductions of PCBs, dioxins and furans in the environment following efforts to eliminate them, in the middle and long term we can expect to see a stabilization and progressive reduction of PBDE levels in atmospheric deposition, house dust, maternal milk, dairy milk and meat.

Due to the high half-life of PBDEs, it could take longer for the accumulated PBDEs in some receiving soils to decline in a significant manner. Some authors have observed bioaccumulation in earth worms in receiving soils (Sellstrom et al., 2005). Of far greater concern however is bioaccumulation in the predatory wildlife of aquatic environments, where the trophic food chain has the greatest number of links (Berryman et al., 2009). On a fat content basis, PBDE levels in fish are 50 times higher than in beef (Schecter et al., 2006). When receiving soils are eroded by runoff they become indirect sources of PBDEs for aquatic environments. But receiving soils are frequently ploughed, reducing concentrations in the surface zone subject to erosion. Moreover, only a small portion of Québec farmland (< 0.5 %) receives biosolids annually, representing less than 0.01 % of the territory of Québec as a whole. In contrast, the atmospheric deposition of PBDEs is considerable, affecting 100 % of the territory. Atmospheric deposition of snow in winter leads an accumulation of contaminants on soil surface that is carried directly into rivers and streams by spring runoff. In comparison, the impact of spreading biosolids is probably negligible in terms of risk to aquatic wildlife.

Conclusion

This study has shown that in a group of Québec dairy farms that are among the most exposed to municipal biosolids, no impact was found on levels in cow's milk of inorganic trace elements including arsenic, copper, molybdenum, zinc and thallium. This confirms the results of a previous study on the safety of recycling Saguenay biosolids on farmland in accordance with Québec regulations, at least with regard to inorganic trace elements. It also invalidates the hypothesis of induced hypocuprosis in cattle due to higher molybdenum input from forage. These results would apply to most Québec dairy farms that receive biosolids, their level of exposure being lower generally than the Saguenay farms examined here, since they are subject to the same restrictions on Mo levels in biosolids.

The analysis results for polybrominated diphenyl ethers (PBDEs) in milk are harder to interpret. The mean levels are statistically higher for the group of 14 farms with biosolids compared to the control group, despite the prohibition against spreading biosolids on pasture land when biosolids are not certified by an independent organization (BNQ). It is possible that when hayfields are harvested, particles of biosolids are picked up by the harvesting equipment. However, a detailed study of the results and a comparison with data in the literature suggest that much of the difference could be attributable to the great variability in factors not controlled by the experimental design. Those factors include exposure to dust in the cowshed and to a lesser degree, forage contamination through the atmospheric deposition of PBDEs.

In terms of environmental health, PBDE levels in milk from farms that use biosolids are still much lower than those reported in the literature for various dairy products, and thus do not contribute significantly to Québec consumers' overall exposure to PBDEs. The same reasoning would apply to the meat produced by these farms. It is also unlikely that the agricultural land application of municipal biosolids is a significant source of PBDE contamination for Québec's water and aquatic wildlife.

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