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POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

Hydrocarbon compounds removal from drinking water using point-of-use devices in emergency

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Mémoire présenté en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

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Présenté par **Elham FEIZI-ASHTIANI**

en vue de l'obtention du diplôme de *Maîtrise ès sciences appliquées*

a été dûment accepté par le jury d'examen constitué de :

Sarah DORNER, présidente
Michèle PRÉVOST, membre et directrice de recherche
Annie CARRIÈRE, membre externe

DEDICATION

To my beloved mom and dad

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RÉSUMÉ

La probabilité de déversement d'hydrocarbures dans les ressources en eau potable augmente au Canada. Les incidents de pipeline, les fuites de réservoirs de stockage ou de canalisations de distribution vers le réseau d'alimentation en eau peuvent causer des dommages considérables à la santé humaine. Les composants les plus hydrosolubles dans l'huile et les produits pétroliers, dont le benzène, le toluène, l'éthylbenzène et les xylènes (BTEX) peuvent provoquer des goûts et odeurs désagréables à faible concentration. L'enjeu avec ces composés est qu'il s'agit de composés cancérogènes et neurotoxiques dangereux pour la santé. Les dispositifs de filtration au point d'utilisation (POU) sont de plus en plus utilisés dans le monde. Ces dispositifs sont peu coûteux et faciles à utiliser et ils offrent, ce qui peut offrir une protection à court terme en cas d'urgence. Ainsi, cette recherche a étudié l'efficacité des filtres domestiques au point d'utilisation (POU) dans l'élimination des composés BTEX comme alternative prometteuse pour accéder à une eau potable propre et sans danger lors de déversements d'hydrocarbures.

Sept unités POU à base de carbone de différents types (deux sous l'évier, deux montées sur robinets, deux systèmes de filtration en pichet et une cartouche de réfrigérateur) ont été testées pour évaluer leurs performances en matière d'élimination de la contamination par l'essence, le diesel et un mélange de BTEX. À l'exclusion des systèmes de filtration en pichet, les autres unités de POU sont certifiées NSF pour la réduction des composés organiques volatils (COV). En plus des allégations de réduction indirecte des COV (par exemple ; le chloroforme en tant que composé de substitution), certaines unités de POU sont certifiées pour retirer le composé individuel de BTEX. Les unités montées sur robinets sont certifiées pour l'élimination du benzène, du toluène et de l'éthylbenzène, et les cartouches de réfrigérateur sont certifiées pour l'élimination du benzène et de l'éthylbenzène, ainsi que la réduction des COV du substitut de chloroforme sous NSF/ANSI53.

Les performances des unités de traitement de l'eau ont été évaluées selon trois tests dans lesquels trois types d'hydrocarbures ont été testés, notamment un mélange de BTEX purs, d'essence et de diesel, afin de prendre en compte les différents types de déversements accidentels susceptibles de se produire et d'être transportés vers une infrastructure d'eau potable. Les essais au laboratoire ont été effectués pour des durées variables, ajustées en fonction de la durée de vie et des débits recommandés par les fabricants des unités POU. Les concentrations dans les affluents ont varié considérablement pour chaque essai et chaque unité au point d'utilisation. Plusieurs facteurs

peuvent influencer les fluctuations de concentration à l’affluent, telles que le contenu en BTEX, l’hétérogénéité des solutions et des flux d'injection, la volatilité des composés BTEX, la sensibilité des carburants à l'adsorption et à la désorption du pilote, les fluctuations de pression et de débit et l'évaporation des BTEX lors de l'échantillonnage. Les concentrations d'affluents testés se situaient entre 353±188 µg/L et 1 201±104 µg/L, entre 553±80 µg/L et 1 856±70 µg/L et entre 106±35 µg/L et 727±90 µg/L dans les essais de BTEX, d'essence et de diesel, respectivement.

Les résultats ont montré que la performance des unités de type POU est liée au type de carburant et aux concentrations initiales en BTEX. Premièrement, lorsque le contaminant est un mélange de BTEX purs dilués dans de l’eau du robinet, les unités les plus prometteuses étaient celles montées sur robinet et les cartouches de réfrigérateurs. Comme prévu, les unités de POU les moins efficaces étaient les systèmes de filtration en pichet qui n’ont pas de certification NSF étaient les unités à transfert. Les absorptions de BTEX étaient de 71% pour le système de filtration en pichet composé de charbon activé granulaire et d'échange d'ions (PT-GAC+IX) et de 85% pour celui constitué de blocs de carbone, d'échange d'ions et de membrane. Néanmoins, les concentrations d'effluents de benzène et de toluène pour ce dispositif n'étaient pas inférieures à la réglementation sanitaire.

Deuxièmement, le filtre sous l'évier contenant des blocs carbone a produit l'eau ayant les plus faibles concentrations de BTEX lorsque l'affluent était composé d’essence diluée dans de l’eau du robinet. Il convient de noter que ce dispositif était efficace pour éliminer le benzène au cours de sa vie utile, et non jusqu'à deux fois sa durée de vie. La teneur élevée de benzène et de toluène dans l’essence a résulté en des concentrations plus élevées de ces composés dans les effluents. Sous les conditions de test, aucune des unités de POU n'a été efficace lorsque les concentrations en BTEX sont plus élevées dans l'affluent. Bien que les concentrations d'éthylbenzène dans tous les effluents étaient plus faible que celles des autres composés de BTEX dans l'essence, les concentrations détectées à l'effluent étaient supérieures au seuil olfactif (1,6 µg/L), mais demeuraient inférieures à la réglementation sanitaire (140 µg/L).

Troisièmement, l’unité POU montée sur robinet et composée de blocs de carbone et de résine a montré les meilleures performances lorsque du diesel dilué dans l'eau potable a été utilisé. Ce dispositif a éliminé 94% des BTEX malgré la présence d'une concentration relativement élevée de BTEX à l'affluent. Toutefois, la concentration de BTEX dans l’affluent avec du diesel étant inférieure à celle de l’essence et du mélange pur de BTEX. Les unités au point d’utilisation apparaissaient plus efficaces pour éliminer les BTEX en présence de diesel, mais cette observation est en partie attribuable aux concentrations plus faibles à l'affluent avec le dosage de diesel. Cependant, les caractéristiques physico-chimiques du diesel pourraient être un facteur de diminution des performances d'élimination (colmatage).

Dans l’ensemble, ce projet a montré que les dispositifs POU certifiés pour l’élimination des BTEX par NSF 53 au cours de leur durée de vie peuvent constituer une solution réaliste, rapide à mettre en place et efficace pour répondre à une contamination de l’eau potable provoquée par un déversement accidentel. Cependant, le choix du dispositif doit être effectué avec soin pour assurer l'élimination des composés les plus toxiques qui font l'objet de normes sanitaires, mais aussi des composés détectables par le consommateur. De plus, le remplacement des appareils après la fin de la contamination doit être géré avec diligence.

ABSTRACT

The likelihood occurrence of the oil spill in drinking water resources is increasing in Canada. Pipeline incidents, leaks from storage tanks or distribution pipeline to the water infrastructure network can cause substantial harm to human health. The most water-soluble components in oil and petroleum products, specifically benzene, toluene, ethylbenzene, xylenes (BTEX), can cause unpleasant taste and odor in low concentration. The concern with these compounds is that they are hazardous carcinogenic and neurotoxic compounds. Nowadays point-of-use (POU) devices have been increasingly used in the world. These devices are inexpensive and easy to use which can address short-term contamination in case of emergency. Thus, this research studied the efficiency of point-of-use (POU) home filters in the removal of BTEX compounds as a promising alternative to access clean and safe drinking water in an oil spill occurrence.

Seven carbon-based POU units with several types (two under-the-sink, two tap-mounted, one refrigerator cartridge, and two pour-through POU units) were tested to examine their performance in the removal of contaminated drinking water by gasoline, diesel, and mixture of pure BTEX. Excluding pour-through filters, other POU units have NSF certification in the reduction of volatile organic chemicals. In addition to the indirect VOC reduction claims (chloroform as a surrogate compound), some POU units are certified to remove the individual compound of BTEX. The tap-mounted units are certified to remove benzene, toluene, and ethylbenzene, and refrigerator cartridge has benzene and ethylbenzene certification, as well as the VOC chloroform reduction surrogate under NSF/ANSI 53.

The performance of the POU units was evaluated according to three assays in which three types of hydrocarbons were tested, including a mixture of pure BTEX, gasoline, and diesel to consider the various probability of accidental spills that could occur and be transported to drinking water infrastructure. The assays were conducted through different test durations adjusted as a function of lifetimes and flow rates recommended by the manufacturers of the POU units. The influent challenge concentrations varied widely for each assay and point-of-use unit. Several factors could affect the influent fluctuations like the inhomogeneity of injecting solutions and flows, the volatility of BTEX compounds, the susceptibility of the fuels to adsorption and desorption to the pilot, fluctuation of pressure and flow and evaporation of BTEX while sampling. The tested influent concentrations were between 353±188 µg/L to 1 201±104 µg/L, 553±80 µg/L to 1 856±70 µg/L and 106±35 µg/L to 727±90 µg/L for BTEX, gasoline and diesel assays, respectively. The results have shown that the performance of POU units is associated with the type of fuels and initial BTEX concentrations. First, for a mixture of pure BTEX diluted in tap water, the most promising POU units were tap-mounted and refrigerator POU units. As expected, the least performance belonged to pour-through units which did not have NSF certification. BTEX removals were 71% for the pour-through composed of granular activated carbon and ion exchange (PT-GAC+IX) and 85% for the one made of carbon block, ion exchange and membrane (PT-IX+CB+NWM). Nevertheless, benzene and toluene effluent concentrations for this device were not below health regulation.

Second, for gasoline diluted in tap water, the most effective POU device was under-the-sink carbon block (US-CB) filter in which the lowest effluent BTEX concentration was observed. This device was performant in the removal of benzene over the operating life, not two times of life. Regarding the high ratio of benzene and toluene in gasoline, this assay provides high concentrations of these compounds in influents. So, the POU units were not effective for benzene and toluene removal if the initial feed is unrealistically high. Although ethylbenzene in all effluent had the lowest ratio among other compounds of BTEX in gasoline, the detected concentrations were more than odor threshold (1.6 µg/L) but less than health regulation (140 µg/L).

Third, for diesel diluted in tap water, the most promising POU unit was tap-mounted composed of carbon block and resin. This device presented BTEX removal greater than 94% for high initial feed. The influent concentration of BTEX was lower than gasoline and a pure mixture of BTEX assays, so the diesel assay reflect more the reality that with mild contamination that point-of-use units would be effective for removal of BTEX. Physicochemical characteristics of diesel could be a factor of declining the removal performance of the devices because they were not able to reduce all the BTEX while the feed concentrations were low. Therefore, an unexpected clogging at 50% of the operating lifetime occurred in the under-the-sink POU device (US-MCM+PAC). Overall, this project has shown that point-of-use devices which are certified for removal of BTEX by NSF 53, over their operating lifetime can be a feasible, immediate, and effective solution for drinking water contamination in an emergency caused by the oil spill. However, the selection of the device should be made carefully to ensure the removal of the most toxic target compounds. Furthermore, the replacement of the devices after the end of the contamination should be managed diligently.

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LIST OF SYMBOLS AND ABBREVIATIONS

AB	Alberta
BE	Benzene
BTEX	Benzene, toluene, ethylbenzene, xylenes
CICEP	Chaire industrielle CRSNG en eau potable
CIS	Cooled injection system
CX	Cation exchange
DW	Drinking water
EB	Ethylbenzene
GAC	Granular activated carbon
GC-MS	Gas chromatography-mass spectrometry
GW	Groundwater
HC	Hydrocarbons
HSSE	Headspace sorptive extraction
HS-SPME	Headspace solid-phase microextraction
IS	Internal standard
IX	Ion exchange
LOD	Limit of detection
LOQ	Limit of quantification
MAC	Maximum acceptable concentration
MB	Manitoba
NEB	National energy board
NSF	National sanitation foundation

NWM	Nonwoven membrane
NWS	Nonwoven screen
ON	Ontario
PAH	Polyaromatic hydrocarbon
PDMS	Polydimethylsiloxane
POU	Point-of-use
PT	Pour-through
PVC	Polyvinyl chloride
PZC	Point of zero charges
QC	Québec
RF	Refrigerator
SBSE	Stir bar sorptive extraction
SK	Saskatchewan
SPME	Solid-phase microextraction
SW	Surface water
TDU	Thermal desorption unit
TL	Toluene
TM	Tap-mounted
TSB	Transportation safety board of Canada
US	Under-the-sink
VOCs	Volatile organic compounds
WHO	World health organization
XE	Xylene

CHAPTER 1 INTRODUCTION

The use of oil and petroleum products in our daily lives increases the occurrence probability of oil spills to drinking water resources or leaks from storage tanks or oil distribution pipeline to the water infrastructure network. Mono-aromatic hydrocarbons benzene related compounds occur naturally in crude oil and its derivatives. They include benzene, toluene, ethylbenzene, xylenes (BTEX). These compounds are considered as the most toxic components of hydrocarbons and are regulated at low levels in drinking water.

Additionally, crude oils contain a considerable concentration of Polycyclic Aromatic Hydrocarbon (PAHs) which are persistent in the environment (Health Canada, 2016). Benzene and several PAHs have been associated with the development of a wide range of cancers (World Health Organisation (WHO), 2017). Benzene being a human carcinogen, it means that exposure to any dosage in drinking water may increase the risk of cancer (Health Canada, 2009).

Thus, many countries have limits in their drinking water standards for many of the compounds. USEPA has proposed a drinking water guideline value for the most hazardous PAH, benzo(a)pyrene of 0.2 µg/l, and 5 µg/l for benzene while the regulation of benzo(a)pyrene and benzene in Quebec are 0.01 µg/L and 0.5 µg/L, respectively (Government of Québec, 2017; Health Canada, 2009, 2016). The presence of these target compounds in the different mixture of hydrocarbons varies widely. The mean mass based percentage content of BTEX is about three percent of crude oil, 22% in gasoline, 12% in diesel, while PAHs are mostly present in crude oil (0,3%) and diesel (0,08%) (Nguyen, 2018).

Traces of hydrocarbons must be removed after an incident of contamination. Adsorption and stripping can be successfully applied for the removal of these contaminants. Point-of-use (POU) filtration devices have been increasingly used in the world (Stalter, O'Malley, von Gunten, & Escher, 2016). In China and the US, around 11-30% of the population use household water purification systems. They are low-cost and easy to use which can provide short-term protection for the community. These home filtration devices are commercially available in different types, including faucet-mounted, pour-through, under-the-sink and refrigerator filters (United States Environmental Protection Agency (USEPA), 2006a). NSF certifications establish the minimum requirements for materials, design, and construction of POU drinking water treatment systems (NSF International, 2016). POU units have been widely used for the removal of manganese, disinfection by-products, toxicity, and dissolved lead from tap water. POU devices are mostly used to remove taste and odor compounds in drinking water (Carrière, Brouillon, Sauvé, Bouchard, & Barbeau, 2011; Deshommes et al., 2010; Stalter et al., 2016; Xie, 2005). In addition to the daily usage of these devices, they can also play the role of temporary remediation for removal of microbiological contaminants in emergencies (Shamsuddin, Das, & Starov, 2014).

Removal technologies in POU devices include granular activated carbon, solid block activated carbon, ion exchange resin, reverse osmosis, and distillation (United States Environmental Protection Agency (USEPA), 2006a). If adsorption is used, these devices are subjected to desorption of organic compounds. Desorption may occur when adsorbed compounds are displaced by more strongly adsorbing compound, or when the concentration gradient in the absorber reverses and adsorbed compound are driven into the water phase by back diffusion (Christopher J. Corwin & Summers., 2010).

The principal objective of this project is the evaluation of hydrocarbons removal performance of activated-carbon-based point-of-use water treatment system that could be deployed in emergency response.

The main research questions that were addressed in this thesis are:

- Can POU devices remove hydrocarbon contaminants from drinking water to meet drinking water standards?
- Which types of POU devices are capable of removing regulated trace hydrocarbons from drinking water?
- Are the NSF volatile organic compounds (VOCs) reduction claims by POUs verified for target BTEX?
- Do the performance of POU units vary for different mixtures of hydrocarbons (BTEX, gasoline, and diesel)?
- Are the fouled POUs susceptible to desorb accumulated contaminants to treated water?

This thesis is structured in 6 chapters: A literature review on the composition of hydrocarbon, hydrocarbon removal methods from drinking water is presented. Then the application of point-of-use devices and the analytical methods in the removal of volatile organic compounds is studied in Chapter 2. The objectives, hypotheses, and methodology are formulated in Chapter 3. Chapter 4 presents the methodology and the performance results of point-of-use units for a mixture of BTEX, gasoline, and diesel diluted in tap water. Finally, conclusion and recommendations are provided in Chapter 5.

CHAPTER 2 LITERATURE REVIEW

2.1 Problem statement

Canadians are among the highest consumers of oil in the world, corresponding to about 4,000 liters of oil per person per year. Also, the rate of oil production in Canada is almost 1.5 times more than its demand (K. Lee et al., 2015). The crude oil and petroleum products are currently shipped by pipelines, rail and truck transport, and tankers across Canada. The Transportation Safety Board (TSB) of Canada reported that over the 2004-2013, 14 pipeline incidents resulting in crude oil spills which are occurred in Canada. Eight of these spills were less than 1 m^3, five were between 1 and 1 000 m^3, and one spill was over 1 000 m^3. Over the past ten years (2006-2015), 26.3 % of pipeline incidents occurred on transmission lines which crossed rivers, streams, and aquifers used as the drinking water supplies (Transportation Safety Board of Canada (TSB), 2016). Even a short duration spill can discharge large amounts of crude oil into the environment and cause significant pollution to ecosystems, downstream communities and human health (K. Lee et al., 2015). Crude oil released into the environment is rarely completely recovered. In most large pipeline ruptures in water, only small amounts of the released oil can be cleaned up (Environmental Defence Canada, Transition Initiative Kenora, & The Council of Canadians, 2016).

Moreover, the transportation of crude oil by rail has recently. According to the recent statement of TSB, over the 2004-2014, an increase in incidents involving the spill of crude oil has occurred, from 500 carloads in 2009 to 160 000 carloads in 2013. The volume of crude oil transported by the truck is less than by pipeline in Canada (Transportation Safety Board of Canada (TSB), 2016).

According to the report titled “Oil Pipeline Safety Failures in Canada,” published by Équiterre, alarmingly, 55% of Québec’s pipeline incidents since 2008 have occurred in 2017 alone, and 86% of those incidents happened on oil pipelines(Environmental Defence & Équiterre, 2017). Figure 2.1 represent data on Québec pipeline incidents from 2008 to 2017. Based on the National Energy Board (NEB) and Transportation Safety Board (TSB) databases from 2008 to 2017, Québec experienced more incidents now than in previous years compared to other provinces. British Columbia with 23.5% had the next highest proportion of incidents in 2017. In Québec, more than 100 pipeline safety incidents occurred which spills of crude oil or refined petroleum products involved over 20%. The total volume spilled amounted to nearly 1 000 barrels (Environmental Defence & Équiterre, 2017).

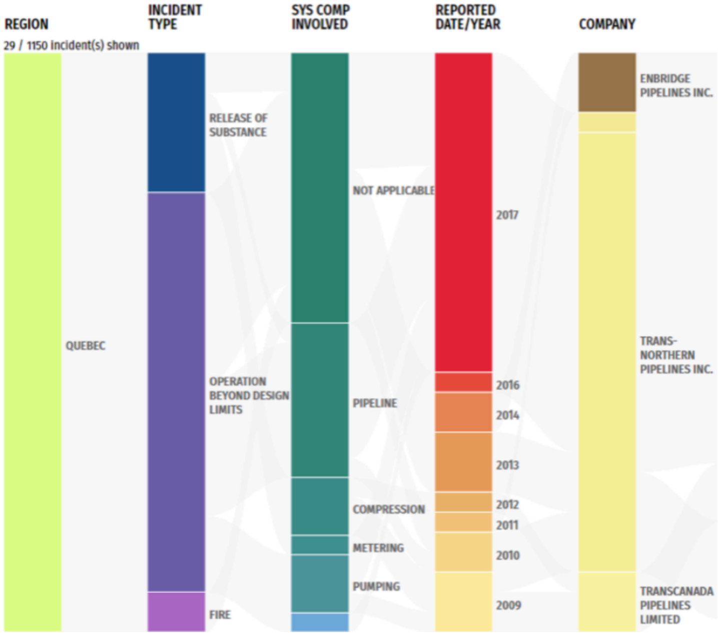


Figure 2.1 Québec pipeline incidents generated from NEB managed pipeline incident data from 2008 to 2017 (Environmental Defence & Équiterre, 2017)

Some of the oil spills across Canada, a summary of volume, the receiving environment, and public environmental effects are explained in the following section.

2.2 Examples of the oil spill in Canada and the United States

In July 2011, 240 m^3 of light crude contaminated Yellowstone River, the drinking water source of nine communities with 125 000 population in Montana, USA. Signs of oil were visible on the river up to 110 km downstream of the spill. The spill was located 24 km upstream of the water intake of one of the communities. The US Environmental Protection Agency (USEPA) promptly contacted municipalities downstream of the spill, and they closed the drinking water intake. The Yellowstone River was exposed to petroleum contamination due to the density of oil pipelines near drinking water intake (ARCADIS U. S., 2011; Atkins North America Inc. & Yellowstone river conservation district council, 2012).

Another significant incident in January 2015 affected the Municipality of Glendive with 6 000 residents. 121m^3 of light Bakken crude was spilled 11 km upstream of the municipality intake water in the Yellowstone River. The contamination extended at least 145 km downstream of the spill location. Two days after the accident, complaints from the public about the odor of oil in drinking water forced the authorities to issue a notice of non-consumption advisory for five days. Bottled water was supplied to the residents. Source water monitoring indicated high benzene concentrations (14 μg/L) far exceeding the US standard in drinking water (5 μg/L). More concerns occurred three months after the spill when the ice melted because the ice cover in winter will diminish benzene volatilization from surface waters. Low temperature along with the presence of ice and snow lead to permeate of oil into void space of snow, reduce the spreading rate and contaminated area. Thus, ice can serve as a natural barrier to the spread of oil. Thus, increasing the temperature can spread pollution in a larger area (Arctic Council, 2015). Abnormal levels of volatile organic compounds were detected in the source water with benzene reaching 2 μg/L. As a result, the plant was shut down for an additional two days (Douglass, 2015; Montana Department of Environmental Quality (DEQ), 2015).

In July 2013, the derailment of a train carrying light crude contaminated the water supply of these Quebec municipalities, namely Saint-Georges, Sainte-Marie and Lévis located at 85 km, 135 km, and 180 km downstream of the spill, respectively. Almost 5 700 m^3 of light crude oil was released to the environment, and 100m^3 of the oil reached to Chaudière River. The municipalities were forced to pre-emptively close their drinking water intake from the Chaudière River until September 18. The same restriction affected companies that drew water from the river. During the preventative closure period, the affected municipalities and companies had to find an alternative source of supply. Temporary pipelines carrying raw water from other sources were installed. This spill affected more than 74 000 residences, and it cost around $ 4.7M (de Santiago-Martín, Guesdon, Díaz-Sanz, & Galvez-Cloutier, 2016).

In January 2015, petroleum odors were detected by consumers in Longueuil drinking water system serving about 300 000 residents. A diesel spill of 28 m^3, had occurred in the treatment plant. A tank supplying diesel to backup emergency pumps for the low-pressure pumping station was completely emptied, and the majority of the spilled fuel flowed through a drain in the city’s sanitary sewer system. Some of the diesel fell into the raw water pumping basin. Although monitoring of water quality at the plant and in distribution network did not exceed drinking water standards, a non-consumption advisory lasting 30 hours was issued. Bottled water was provided to citizens costing more than $740 000 (Champagne, 2015; Ouimet, 2015).

In July 2016, a ground movement ruptured the pipelines carrying diluted heavy crude oil and 225 m^3 of diluted bitumen spilled on land 160 m from the south shore of the North Saskatchewan River. The flow of the river was high, and the oil plume traveled downstream for more than 370 km till four days after the spill. A situation assessment and sampling program were immediately implemented, and more than 2 500 samples were collected and analyzed across 550 km in three days. At 120 m of the spill location, benzene concentration exceeded the criteria of the Canadian drinking water; at 380 km downstream of the spill, 14 exceedances of benzo[a]pyrene were recorded. The presence of other potentially hazardous compounds such as toluene, ethylbenzene, xylene, and several PAHs was detected over 200 km. A restriction on the use of water was issued, and the water intake was shut down. A ban on using the North Saskatchewan River by the municipalities with a water intake downflow of the spill was then issued. These municipalities included North Battleford (14 000 residents) 124 km downstream of the discharge, Prince Albert (35 000 residents) 380 km and Melfort (6 000 residents) 546 km downstream. The ban was maintained for almost two months after the spill (Franson, 2016; Government of Saskatchewan, 2017).

2.3 Chemical composition and properties of petroleum hydrocarbons

Crude oil is complex and contains different mixtures of chemicals. Despite wide variation in chemicals composition of crude oil, their primary compositions include: carbon (84-87%), hydrogen (10-14%), nitrogen (0.1-2.0%), oxygen (0.05-1.5%) and sulfur (0.05-6.0%). Hydrocarbon compounds are the composition of hydrogen and carbon, which are the main elements in crude oils. They are combined with other elements ranging from smaller, volatile compounds to large, non-volatile compounds. Petroleum products such as gas and diesel fuel are a mixture of refined and fewer compounds with specific standards. Each oil has a unique structure that usually includes four major classes of chemicals: saturated hydrocarbons, aromatics, resins, and asphaltenes (Fingas, 2015).

Saturated hydrocarbons are the major components of petroleum considered the least toxic fraction of the four main petroleum fractions. Aromatic hydrocarbons are cyclic, unsaturated compounds and their structures are based on a single benzene ring (C_6H_6) or multiple benzene rings which named mono- or polyaromatic hydrocarbons. The most common mono-aromatics in petroleum are the BTEX series consists of benzene, toluene, ethylbenzene, and the three xylene isomers. Benzene, ethylbenzene, and toluene are considered as priority pollutants on the USEPA list of toxic chemicals. The most water soluble of hydrocarbons are monoaromatics that may cause acute toxicity. These compositions are light enough to be volatile and flammable so can cause breathing hazards. Polyaromatic hydrocarbons (PAHs) are less volatile and more persistent than monoaromatics due to having two or more aromatic rings (Code of Federal Regulations (CFR), 2012; K. Lee et al., 2015).

Whereas the structure of several saturated and aromatic compounds is identified and has been studied, individually or in an oil matrix. Resins are polar compounds with an unknown composition having one or more S-, N- and O- heteroatoms. Similar to resins, the structure of asphaltene molecules have not been determined. Due to the complexity of their structure, it is impossible to derive a formula for these compounds in the scope of available methods. It would be described in terms of several structural types rather than a fixed molecular structure. Overall, they have a higher molecular weight, greater aromatic content and are less polar than resins (K. Lee et al., 2015). Table 2.1 shows the composition of petroleum products and some typical crude oils.

Table 2.1 Typical composition of some crude oil and petroleum products (Fingas, 2015)

Group	Compound class	Gasoline	Diesel	light crude	Heavy crude
Saturates		50–60	65–95	55–90	25–80
	Alkanes	5–55	35–45	40–85	20–60
	Cycloalkanes	5	25–50	5–35	0–10
Olefins		5–10	0–10		
Aromatics		25–40	5–25	10–35	15–40
	BTEX	15–25	0.5–2.0	0.1–2.5	0.01–2.0
	PAHs		0–5	10–35	15–40
Polar compounds			0–2	1–15	5–40
	Resins		0–2	0–10	2–25
	Asphaltenes			0–10	0–20
Sulfur		0.02	0.1–0.5	0–2	0–5
Metals (ppm)				30–250	100–500

2.3.1 Sources and environmental fate of BTEX

Benzene is found naturally in the environment at lower concentrations comparing its sources caused by human activity. Toluene, ethylbenzene, and xylenes are primarily synthetic compounds that exist in petroleum products, such as crude oil, gasoline, and diesel fuel, or used as industrial solvents or benzene production. The BTEX components are the most soluble and mobile fraction of crude oil and petroleum products, and per se, typically enter the soil, sediments, and aquatic environments because of accidental spills, leakage of petroleum fuels from storage tanks, pipeline ruptures, and chemical waste discharge. Thus, accidental releases of these compounds may have an inevitable consequence in the environment and public health (Health Canada, 2014).

Health Canada environmental monitoring results are available for benzene in surface water and groundwater. Surveillance results show that, when detected, levels are less than 1 µg/L. Benzene has only affected some groundwater supplies in Canada and owing to the easily evaporating. It might not be a concern for Canadians who use surface water as the source of drinking water. However, the presence of an ice cover in winter may increase that risk because it will diminish benzene volatilization from surface waters (Health Canada, 2009).

Concerning toluene, ethylbenzene, and xylenes, monitoring results show undetectable or low levels of these chemicals in most Canadian drinking water supplies. Canadians are more exposed to toluene, ethylbenzene, and xylenes through the air than drinking water, although it can be considered a source of contamination (Health Canada, 2014). The concentration of BTEX in petroleum-hydrocarbon contaminated groundwater caused by gasoline and diesel fuel leakage is considerable. Meanwhile, some researchers suggest that the spilled BTEX could be biodegraded. Monitoring results show that BTEX concentrations decrease with a first order rate of 5.4×10^{-4} d^{-1} along the transport path (Chiu, Hong, Lin, Surampalli, & Kao, 2013). Some examples of benzene, toluene, ethylbenzene and xylenes levels measured in different water supplies and drinking water in Canada have been summarized in Table 2.2.

Table 2.2 BTEX concentration in water supplies in Canada (AB-Alberta, SK-Saskatchewan, QC-Québec, ON-Ontario, CA-Canada, MB-Manitoba, NB-New Brunswick, SW-surface water, GW-ground water, DW-drinking water)

Contaminant	Mean Concentration (μg/L)	Maximum Concentration (μg/L)	Location	Year	Media	Explanation	Reference
Benzene	0.28	4.92	AB	1998–2005	Treated SW	30 samples from 26 locations	(Health Canada, 2009)
	0.097	0.23	AB	1998–2006	Treated GW	15 samples from 11 locations	
	0.25	1	SK	1995 – 2005	Treated DW	30 samples from 9 locations	
	071	1 700	SK	1995 – 2005	Treated GW	34 samples from 13 locations	
	0.35	0.36	QC	2001 – 2005	Treated DW	2 362 Samples were reported below LOD (0.03–2 μg/L)	
	0.05 – 0.2	–	ON	2002 2008	SW and GW	2 277 treated water samples	
	–	0.35	ON	2002 2008	Untreated SW	2 762 raw water samples	
	–	155	ON	1991	Untreated SW	St. Marys River, Ottawa River	
	0.38	–	AB	1984	Untreated SW	SW	
	1.87	82	QC	2012	GW	Among 21 samples, except two samples, all other samples were below detection limit	(Institut national de la santé publique du Québec (INSPQ), 2013)
Toluene	2.00	–	CA	1979	Treated DW	Sampling from 30 water treatment facilities	(Health Canada, 2014)
	< 0.5	–	ON	1975	Untreated water	Sampling in Great Lakes (GW, lake and river water)	
	–	20	ON	2007–2012	Untreated water	Among 46 472 samples from lakes and rivers, 62 samples were above 0.5 μg/L	
	–	22	MB	2007–2012	Untreated water		
	–	1.3	NB	2003–2012	Treated DW	Detected in 1% of DW over 5 000 samples	
	–	2	QC	2002–2012	Untreated water		
	>1	3 300	SK	1989–2012	Treated DW	Contamination levels above one μg/L in 44 of 321 samples of treated DW	(Government of Canada, 1992)
	–	22	SK	2002–2012	Treated DW		
	–	730	ON	1987	GW	Sampling from wells near waste disposal sites.	

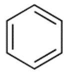
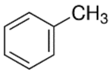
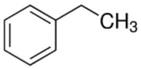
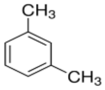
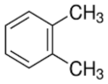
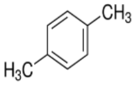
Table 2.2 BTEX concentration in water supplies in Canada (AB-Alberta, SK-Saskatchewan, QC-Québec, ON-Ontario, CA-Canada, MB-Manitoba, NB-New Brunswick, SW-surface water, GW-ground water, DW-drinking water) (continued)

Contaminant	Mean Concentration (µg/L)	Maximum Concentration (µg/L)	Location	Year	Media	Explanation	Reference
Ethylbenzene	–	5.5	MB	2007–2012	Untreated water		(Health Canada, 2014)
	–	1.4	NB	2003–2012	Treated DW	It has been detected in 1.5% of DW over 5 000 samples	
	–	0.12	QC	2002–2012	Untreated water		
	–	550	SK	1989–2012	Treated DW	Five sites in the Niagara Falls area	
	541	–	ON	1997	Untreated water	56 GW samples near gasoline stations	
	–	3 320	ON	1988	Untreated GW	GW at 5 of 6 southern ON landfills	
	–	120 000	ON	1990	Untreated GW	monitoring wells installed beside or into former waste disposal lagoons	
	–	0.15	ON	2007–2008	SW	St. Clair River	(Environment and Climate Change Canada, 2016)
	–	1.50	ON	2005	GW	Sampling from wells brownfield sites in Ottawa and Toronto	
Xylenes	–	30	MB	2007–2012	Untreated water	o-xylene	(Health Canada, 2014)
	–	75	NB	2003–2012	Treated DW	It has been detected in 1.1% of DW over 5 000 samples	
	–	013	QC	2002–2012	Untreated water	o-xylene	
	–	021	QC	2002–2012	Untreated water	m/p- xylene	
	–	2 825	SK	1989–2012	Treated DW	xylenes	
	–	21	ON	1990	GW	o-xylene was measured in 8 test wells	(Government of Canada, 1993)
	–	50	ON	1990	GW	m/p-xylene was measured in 8 tests	
	–	123	CA	1987	GW	Sampling from wells near beneath landfill sites (o-xylene)	
	–	191	CA	1987	GW	Sampling from wells near or beneath landfill sites (m/p-xylene)	
	325	374	CA	1991	GW	Sampling from wells near site formerly used for the disposal of liquid industrial waste	
	–	1 700	CA	1990	GW	Sampling from wells near an active industrial chemical waste disposal lagoon	
	–	3 100	CA	1990	GW		

2.3.2 Identification and physical-chemical properties of BTEX

Benzene is the simplest homolog of the aromatic hydrocarbons with the molecular formula C_6H_6. The structure of the molecule is composed of 6 carbon atoms arranged in a regular hexagon attached to one hydrogen atom each. It is a volatile, colorless liquid with a characteristic odor. Toluene, ethylbenzene, and xylenes are colorless, volatile, flammable, and liquids with a sweet, gasoline-like odor. According to Health Canada, all three compounds have characteristics of mono-aromatic hydrocarbons, and they are by-products of benzene. Toluene and ethylbenzene differ from benzene by adding a single methyl or ethyl group, respectively, while the substitution of two methyl groups forms the xylenes structure. The different position of the methyl groups on the benzene ring define of isomers xylene: ortho- (o-), meta- (m-) or para- (p-) xylene. Typical mixtures of xylenes composed of approximately 40% m-xylene, 24% o-xylene and 19% p-xylene, as well as 17% ethylbenzene (Health Canada, 2009, 2014). Table 2.3 shows the chemical-physical characteristics of BTEX. Njobuenwu et al. in 2005 showed in a model that benzene with greater solubility in water has the largest dissolution rate, while o-xylene with the biggest density has the lowest solubility in water. Benzene water solubility is about 2.6 and 20.6 times more than the solubility of toluene and ethylbenzene, but with a different proportion with the xylenes (Njobuenwu, Amadi, & Ukpaka, 2005).

Table 2.3 Chemical-physical characteristics of BTEX (U.S. National Library of Medicine, 2014)

Properties	Units	Benzene	Toluene	Ethylbenzene	m-xylene	o-xylene	p-xylene
Chemical Structure							
Molecular Formula	-	C6-H6	C7-H8	C8-H10	C8-H10	C8-H10	C8-H10
Molecular Weight	gmol^{-1}	78.11	92.139	106.165	106.165	106.165	106.165
Solubility (25^{o} C)	mgL^{-1}	1790	526	170	161	178	162
LogKow	-	2.13	2.73	3.15	3.2	3.12	3.15
Henry's law constant (25^{o} C)	Pa m^{3}mol^{-1}	556	664	788	718	518	690
Boiling Point	°C	80.08	110.6	136.2	139.1	144.5	138.3
Density (20^{o} C)	gcm^{-3}	0.876	0.862	0.862	0.869	0.88	0.861
Vapor Pressure (25^{o} C)	mm Hg	94.8	28.4	9.6	8.29	6.65	8.84

2.3.3 Regulations and guidance in drinking water

The types of standardized hydrocarbon compounds and the maximum acceptable concentrations vary according to countries, provinces, and regulatory organizations. Because of the epidemiological evidence and bibliography available on their toxicity, the most severely regulated compound among BTEX compounds is benzene. Established standards aim to minimize chronic long-term exposure to the targeted contaminant. Maximum acceptable concentrations are extrapolated from epidemiological studies or animal studies adjusted by human conversion factors. Values are generally normalized for acceptable risk after an exposure of 70 years with daily consumption of 1.5 to 2 liters (Nguyen, 2018). Health Canada classification considers benzene to be a human carcinogen. Studies indicate that the exposure of benzene by both animal and human have similar toxic effects. The maximum acceptable concentration (MAC) for benzene in drinking water is defined through the incidence of cancer in mice, based on the calculation of a lifetime unit risk. It is a concentration at which the cancer risk is considered negligible.

According to Health Canada, there is currently inadequate information to determine the carcinogenic potential of toluene for both animal and human, although some studies indicate neurological effects in animal and human for both acute and chronic exposure. The symptoms include loss of color vision, disturbances in concentration, mental function, and memory over the long-term inhalation of toluene. Ethylbenzene is classified as possibly carcinogenic to humans, based on sufficient sign of cancer in animals but insufficient data in humans. Xylenes are not in the category of carcinogenicity in humans, due to the lack of information (Health Canada, 2009, 2014).

Health Canada and the World Health Organization (WHO) provide recommendations for all BTEX. Health Canada set maximum acceptable concentrations (MACs) for BTEX ranging from 5 μg/L to 140 μg/L depending on the compound (Health Canada, 2009, 2014). Threshold concentrations defined by the WHO is much higher (from 10 μg/L to 700 μg/L) (World Health Organization (WHO), 2011). The Quebec standard for benzene is the most stringent at 0.5 μg/L (Government of Québec, 2017), much lower than the federal standard in the US of 5 μg/L (United States Environmental Protection Agency (USEPA), 2012). The differences observed between benzene standards can be explained by differences in risk calculations, but also by the date at which these standards and recommendations were revised. Indeed, the less stringent American standard of benzene dates back to 1998 but has been maintained after six-year review progress, but the maximum contaminant level goal is set at zero. The American standard of benzene (5 μg/L) is based on a risk of leukemia for life within 2.2-8.0*10^{-6}. Health Canada established benzene recommendation (5 μg/L), based on daily drinking water exposure (dermal, inhalation and consumption) of 3.5 L and a lifetime cancer risk 10^{-5} (Health Canada, 2009). The INSPQ recommendation is also based on this study, but adjusting daily intake to 2 L/day and a lifetime cancer risk at 10^{-6}, setting a standard of 0.5 μg/L (Institut national de la santé publique du Québec (INSPQ), 2013).

Table 2.4 summarizes regulations of drinking water for BTEX in Quebec, Canada, the United States and the WHO (Government of Québec, 2017; Health Canada, 2009, 2014; United States Environmental Protection Agency (USEPA), 2012; World Health Organisation (WHO), 2017).

Table 2.4 Regulation of drinking water for BTEX in Quebec, Canada, USEPA and WHO (μg/l)

Substances	Quebec	Health Canada			USEPA	WHO		
	Health	Health	Taste	Odor	Health	Health	Taste	Odor
Benzene	0.5	5	4 680	500-4500	5	10		10 000
Toluene	-	60	140	24	1 000	700	40-120	24-170
Ethylbenzene	-	140	72	1.6	700	300	72-200	2-130
Xylenes	-	90		20	10 000	500	300	20-1 800

Maximum concentration of industrial wastewater and municipality sewage treatment plants discharged to surface water is regulated. Discharge permits vary across industrial categories and are set considering the performance of treatment and control technologies present at the emitter location and the wastewater plant. For example, allowable concentrations or loads are set for discharge into the sanitary and combined sewer in Toronto and the Communauté Urbaine de Montréal (CMM). Table 2.5 summarizes the BTEX regulations for wastewater discharges set by Montreal, Toronto, and Canada. In the United States, the national regulatory standards are based on total maximum daily load (TMDL) which is calculated according to the classification of water supply, location surface water, the location of industry or municipal in the river (upstream or downstream).

Table 2.5 Regulation of wastewater discharge for BTEX in Montreal, Toronto and Canada (µg/l) *(Ministère de l'Environnement et de la Lutte contre les changements climatiques (MELCC), 2015)*

Substances	Montreal Physical-chemical	Toronto	Canada
Benzene	500	10	10
Toluene	400	16	24
Ethylbenzene	400	160	60
Xylenes	700	1400	300

2.4 Processes to remove BTEX compounds from water

Aromatic organic compounds such as BTEX are present in crude oil at different percentage and concentrations. Since these organic compounds are categorized as toxic, carcinogenic, and/or mutagenic chemicals, their presence in water supplies even at low concentration is a critical public health concern. Thus, ensuring the absence of these organic compounds in source water and consequence in drinking water is crucial for the safety in public health (Herman Hindarso, Suryadi Ismadji, Filicia Wicaksana, Mudjijati, & Indraswati, 2001; Redding, Burns, Upson, & Anderson, 2002).

The presence of BTEX in water bodies is mainly due to the accidental oil spills and wastewater effluent from chemical process industries. Numerous research has been carried out in the past years on BTEX removal from drinking water and wastewater. Many methods such as chemical oxidation, biological treatment, air stripping, membrane separation, condensation, and adsorption have been used successfully for BTEX removal from wastewater. The most widely used and most efficient method is adsorption. Several approaches have been reported in the literature for the removal of oil from water contaminated with fuel oil by using several naturals, hydrophobic and large surface area sorbents (Wibowo, Setyadhi, Wibowo, Setiawan, & Ismadji, 2007).

Studies are in progress worldwide for promoting cost-effective technologies using enhanced sorption material for the removal of organic compounds from oil-contaminated water. For this reason, among various type of absorbent, activated carbon is a justified, authentic alternative for removal of low concentration of aromatic hydrocarbon from water or wastewater (Adachi, Ozaki, Kasuga, & Okano, 2006). Also, the US Environmental Protection Agency has cited adsorption onto activated carbon as a first-rate available environmental control technology (United States Environmental Protection Agency (USEPA), Office of Emergency and Remedial Response, & Development, 1991).

Activated carbon is one of the main microporous adsorbents. Owing to its large surface area, a wide-ranging pore sizes, a variety of impurities and irregularities, activated carbon has a complex structure. All these variations in the characteristics of activated carbons depend on the precursor materials used and the different preparation methods. Therefore, characterization of the pore structure of the activated carbons plays an essential role in adsorption and separation processes (El-Sayed & Bandosz, 2004; Ismadji & Bhatia, 2001).

One of the significant factors in controlling the adsorption process of organic carbon in aquatic is the pH of the solution. The solution pH affects the ions on the carbon surface. The point of zero charges (PZC) refers to the pH value at which the charge density of the ions at the surface equals zero. At pH values below the PZC, the solution donates more protons (H^+) than hydroxide groups (OH^-). Thus, the adsorbent surface is positively charged.

On the contrary, at pH values above the PZC, the adsorbent surface is negatively charged. Investigated benzene removal by activated carbon adsorption from aqueous solutions at different pH values (3, 7, and 11) and determined that the adsorption capacity increases with pH value. This trend was validated for three activated carbons with a different range of pH (Wibowo et al., 2007).

2.5 Point-of-use (POU) treatment technologies

It is estimated that around 11-30% of Chinese and Americans use home filtration devices and 90% of Korean avoid using tap water (Stalter et al., 2016). Italy and Germany are the largest consumers of bottled water among Europeans with a consumption of 188 and 175 liters per capita in 2017 (European Federation of Bottled Waters (EFBW), 2017). Point of Use (POU) devices treat water at a point of use within the house and are useful for the removal of contaminants that pose a risk through ingestion. POU devices are designed for the purification of only the portion of water that is used for drinking and cooking purposes. These home filtration devices are commercialized in several types, including faucet-mounted, pour-through, under-the-sink and refrigerator filters. Faucet-mounted devices are connected to the faucet or sit on the counter with connections to the faucet. Pour-through types (such as pitchers with a filter) are the simplest category of activated carbon filter water is poured through the carbon and collected in a container. These types will not connect to the water supply. Both faucet-mounted and pour-through categories are inexpensive and user-friendly, but they can treat only limited quantities of water at a time. Because of the low amounts of activated carbon available in the device which can provide limited contact time (United States Environmental Protection Agency (USEPA), 2006b).

These devices are low-price and user-friendly so that they can provide short-term protection during contamination emergencies. They prove useful in an effective and quick response to provide safe and unpolluted drinking water through guideline and standards. In 2008, the U.S. EPA launched a research program for the evaluation of the performance of numerous POU for the treatment of tap water in houses, or as a temporary remedy during accidental contamination. Work conducted at the Test & Evaluation Facility focused on measuring the efficiency of three different POU units for removal of microbiological contaminants in drinking water. The technology of the POUs was based on filtration through electrostatically charged media and reverse osmosis membrane. The systems were challenged with several microbiological contaminants including *E. coli, Cryptosporidium*, MS2 bacteriophage, and polystyrene latex beads. The results showed that these POU systems have effectively removed the target biological contaminants (Sinha et al., 2008).

Carrière et al. (2011) examined the performance of the pour-through and under-the-sink POU systems using cationic exchange resins for reduction of dissolved manganese concentration in drinking water. They evaluated these devices for both low and high (100 µg/L, 1 000 µg/L) influent manganese concentrations. Owing to the 60% at 100% rated capacity, and greater than 45% at 200% of the lifetime of the pour-through filters, this type of POU was identified as the most effective POU in the removal of dissolved manganese with the concentration of 1 000 µg/L. Under-the-sink filters were efficient in the removal of dissolved manganese, but over a shorter operating time because of the competition of other cations such as hardness. According to this study, the filters with activated carbon block system and other technologies were not efficient in removal dissolved manganese (Carrière et al., 2011).

Deshommes et al. (2010) conducted the reduction of lead and other metals by using four types of POUs including pour-through, tap-mounted (2 types) and under-the-sink devices. In this study, four experiments were carried out, and the reduction of lead by pour-through POU devices was evaluated. Due to the presence of lead in influent, the efficiency of POU in lead removal was lower than those identified by the manufacturers. The effect of dissolved lead in influent was examined as well. In the presence of significant particulate lead, the pour-through POU devices were ineffective because total lead concentration in effluent surpassed the NSF lead threshold (10 µg/L).

Consequently, the pour-through filters were not efficient for removal of particulate lead. All types of examined POUs (except pour-through) were effective in removing particulate lead. Moreover, they indicated the pour-through POUs with the technology of cation exchange (CX) resin removes dissolved lead more effectively than POU devices composed of granular activated carbon (GAC). Moreover, their performances were higher for particulate lead (96-99%) than for dissolved lead removal (80-94%). Regarding the efficiency of POUs in the removal of metal, copper was removed successfully at the concentration tested, and silver concentrations remained below the secondary MCL of 0.1 mg/L (Deshommes et al., 2010).

2.6 NSF/ANSI standard for drinking water treatment units

While no regulations exist for residential water treatment filters, purifiers, POU and POE systems, voluntary national standards and NSF International protocols have been established minimum requirements for the safety and performance of these products to treat drinking water. The standards and protocols studied in this project are NSF/ANSI42 and NSF/ANSI53. Point-of-use units certified by NSF 42 reduce aesthetic impurities such as chlorine and taste/odor and filters certified by NSF 53 have claims of removal for contaminants with a health effect. Health effects are established in this standard as regulated by the U.S. Environmental Protection Agency (EPA), Health Canada or any U.S. Federal Regulations.

Standards NSF 42 and NSF 53 both cover adsorption/filtration. The processes capable of removing organic compounds in the pores of or to the surface of, an adsorbent media. This Standard consist of activated carbon filter systems. This section provides minimum requirements for materials, test method, and performance of point-of-use drinking water treatment systems addressed by this standard for the reduction of volatile organic compounds with special attention on BTEX (NSF International, 2016).

2.6.1 Water supply characteristics

According to the NSF protocol, Table 2.6 presents specific characteristics of the public water supply that shall be used and maintained throughout the test for contaminant reduction claims:

Table 2.6 General characteristics of water testing for contaminant reduction claims specified by NSF protocol (NSF International, 2016)

Total dissolved solids (TDS)	200 -500 mg/L
Total organic carbon (TOC)	> 1.0 mg/L
Temperature	20 ± 2.5 °C
Turbidity	< 1 NTU
pH	7.5 ± 0.5

2.6.2 Minimum service flow

The minimum initial clean-system flow rates presented in Table 2.7 are specified by NSF protocol for the point-of-use systems connected to the pressurized line. The minimum flows shall be achievable by the system at an inlet pressure of 30 psi and a water temperature of 20 ± 3°C, with a fully open outlet. No minimum service flow has been specified for pour-through systems and particular systems like glass filter and ice maker for the refrigerator.

Table 2.7 Minimum service flow rates recommended by NSF 53 standard for the point-of-use systems (NSF International, 2016)

Type of POU	**Minimum service flow**
Countertop connected to sink faucet with diverter	0.8 L/min
Faucet mount with diverter	0.8 L/min
Faucet mount without diverter	1.9 L/min
Plumbed in	1.9 L/min
Plumbed in to separate tap with the reservoir	7.6 L/min
Plumbed in to separate tap without reservoir	0.8 L/min

2.6.3 Minimum performance requirement

According to the NSF protocol, if the POU unit includes a performance indicator, the indicator shall be equipped with an automatic, operative means to warn the user when the system is not carrying out its chemical reduction function. The acceptable activation range shall be within -20% to 10% of the manufacturer’s claimed capacity. These systems should be tested to 120% of their rated capacity for reduction of claimed chemicals and the POU units without performance indicator shall be evaluated to 200% of their rated capacity for removal of claimed compounds (NSF International, 2016).

2.6.4 Chemical reduction claims

In NSF 53 standard, two approaches have been taken when developing contaminant reduction claims for water treatment filters: direct measurement of VOC and VOC reduction surrogate testing. An indicator or surrogate compound used for indirect measurements of activated carbon adsorption should be less well-removed. Thus, it will break through first to ensure that the indirect measurement does not result in an overstatement of claims. According to NSF 53 protocol, chloroform is a good potential surrogate compound for several organic contaminants due to the low molecular weight and high water-solubility and therefore this compound is less well-removed from water by activated carbon than many other compounds.

Surrogate claims for chemical reduction are suggested for a group of organic chemicals. Benzene, toluene, ethylbenzene, and xylenes are included in this group. According to the NSF protocol, the point-of-use systems shall reduce the mean influent concentrations of chloroform (300 ± 30 μg/L) at least 95 percent. Table 2.8 Show the surrogate organic reduction testing condition, including drinking water regulatory level, influent challenge concentration, chemical reduction, and maximum product water concentration. Direct organic reduction testing with individual organic contaminants is the other approach possible with the NSF protocol. Actual laboratory data are desirable to confirm the chloroform surrogate testing results. Thus, some POU units are certified for both the surrogate and individual organic reduction claims.

Table 2.9 shows the chemical reduction requirements of direct organic reduction testing, including influent limits, average influent challenge concentration, maximum effluent concentration, and USEPA methods. Device certified by NSF 53 for removal of volatile organic compounds, based on both direct and surrogate measurement, might not be sufficient to remove for the case of BTEX from spills in drinking water. Thus, in studies aims to evaluate the performance of the point-of-use device for removal of the BTEX in case of fuel spill to drinking water (NSF International, 2016).

Table 2.8 Surrogate organic reduction testing condition, including drinking water regulatory level, influent challenge concentration, chemical reduction and maximum product water concentration (NSF International, 2016)

Compounds	Drinking water Standards (mg/L)	Influent challenge concentration (mg/L)	Chemical reduction (%)	Maximum effluent water concentration (mg/L)
Benzene	0.005	0.081	> 99	0.001
Toluene	1	0.078	> 99	0.001
Ethylbenzene	0.7	0.088	> 99	0.001
Xylenes	10	0.07	> 99	0.001

Table 2.9 Chemical reduction requirements of direct organic reduction testing, including influent limits, average influent challenge concentration, maximum effluent concentration and USEPA methods (NSF International, 2016)

Compounds	Individual influent limits (mg/L)	Average influent challenge (mg/L)	Drinking water Standards (mg/L)	USEPA method(s)
Benzene	0.015 ± 30%	0.015 ± 10%	0.005	502.2, 524.2, 524.3
Toluene	3.0 ± 30%	3.0 ± 10%	1	502.2, 524.2, 524.3
Ethylbenzene	2.1 ± 30%	2.1 ± 10%	0.7	502.2, 524.2, 524.3
Xylenes	14.4 ± 30%	14.4 ± 10%	10	502.2, 524.2, 524.3

2.7 Analytical methods to quantify trace hydrocarbons

Several analytical methods can be used to identify and quantify BTEX compounds in aqueous matrices. All require a form of sample preparation and extraction for low concentration samples. The most commonly used methods are purge-and-trap and microextraction techniques coupled with gas chromatography-mass spectrometry. Purge and trap method is a dynamic headspace technique which reduces the effect of the matrix and enhances sensitivity. Samples containing VOCs are placed into a purging container then Helium as a noble gas is passed through the sample at a constant flow rate and specified time. Volatile compounds are extracted from the sample into the headspace above the sample and are transferred to an adsorbent trap. After the completion of the purging procedure, the trap is rapidly heated and backflushed with the carrier gas to desorb and transfer the analytes to the GC column (Centre d'expertise en analyse environnementale du Québec (CEAEQ), 2014).

Belardi and Pawliszyn in 1989 presented the best-known microextraction technique known as solid-phase microextraction (SPME) (Belardi & Pawliszyn, 1989). By using a fiber coated with polydimethylsiloxane (PDMS) as the extraction phase, analytes can be analyzed through immersion in sample or headspace mode (Laaks, Jochmann, & Schmidt, 2012b; Sieg, Fries, & Puttmann, 2008).

The extraction technique implies the sorption of different range of high to low-volatility compounds into the PDMS coated fiber then introduced by thermal desorption into the gas chromatography-mass spectrometry for analysis. The main subject of the application of microextraction techniques depends on the characteristics of the analytes. For instance, stir bar sorptive extraction (SBSE), is mainly used for medium to low-volatility compounds which can merely be extracted directly from liquid matrix while high capacity headspace sorptive extraction (HSSE) is mostly limited to the analysis of volatile and semi-volatile compounds (Tienpont, David, Bicchi, & Sandra, 2000).

Recent analytical developments aim for full automation and solvent exclusion methods in the analysis of organic compounds. In the analysis of benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds, the detection limits for solvent-free techniques are in low ng/L range and with relative standard deviations below 10% (Laaks, Jochmann, & Schmidt, 2012a). M. R. Lee, Chang, and Dou (2007) improved the trace BTEX analytical method in water by using cryo-trap equipment in headspace solid-phase microextraction coupled to gas chromatography-mass spectrometry (HS-SPME-GC/MS). The proposed analytical method (SPME-cryo-trap-GC/MS) reached at sub-ng/L levels for limits of detection (LOD) of each analyte (M. R. Lee et al., 2007).

The method used in this study was developed and optimized on a headspace sorptive extraction (HSSE) system. Headspace sorptive extraction is a hybrid development of stir bar sorptive extraction (SBSE) that mimics the solid-phase microextraction (SPME) in the gas phase. Thus, samples collected for the mixture of BTEX and gasoline assays were analyzed by HSSE-GC/MS technique, and samples of diesel assays were analyzed by purge and trap-GC/MS (Pastor-Belda, Viñas, Campillo, & Manuel, 2019; Tienpont et al., 2000). Table 2.10 presents the limit of detection of the discussed methods.

Table 2.10 Limit of detection (µg/L) of purge and trap-GC/MS, SPME-cryo-trap-GC/MS, HS-SPME-GC/MS and HS-SBSE-GC/MS methods ((Centre d'expertise en analyse environnementale du Québec (CEAEQ), 2014; Cho, Kong, & Oh, 2003; M. R. Lee et al., 2007)

Analyte	**Limit of detection of methods**			
	purge and trap-GC/MS	**SPME-cryo-trap-GC-MS**	**HS-SPME-GC-MS**	**HS-SBSE-GC-MS (CICEP)**
Benzene	0.080	0.040	0.066	0.031
Toluene	0.060	0.020	0.038	0.028
Ethylbenzene	0.080	0.050	0.022	0.016
o-xylene	0.080	0.020	not determined	0.013
m-xylene		0.100		0.078
p-xylene				

CHAPTER 3 RESEARCH OBJECTIVES, HYPOTHESES AND METHODOLOGY

3.1 Research objectives and hypotheses

This project aims at assessing the effectiveness of point-of-use (POU) devices for the removal of hydrocarbon (HC) from tap water. Specifically, the application of these devices in emergency cases where the petroleum hydrocarbon spill has occurred in the drinking water sources and distribution system.

The detailed objectives of this project are to:

1. Determine the efficiency of POU devices (under-the-sink, tap-mounted, refrigerator and pitcher filters) for the removal of trace hydrocarbons contaminants.
2. Compare the effect of different mixtures of HCs (a mix of BTEX with gasoline and diesel) on the removal performance of POU devices
3. Verify the NSF organic chemical claims for these devices
4. Investigate whether POU treatment devices are susceptible to desorption of accumulated contaminants.

Realizing these objectives will allow us to answer essential questions concerning the suitability of POUs as a temporary alternative in the case of contamination of drinking water by a fuel oil spill.

- Can POU devices remove hydrocarbon contaminants from drinking water to meet drinking water standards?
- Which types of POU devices are capable of removing trace HC from drinking water?
- Are the NSF volatile organic compounds (VOCs) reduction claims by POUs verified for target BTEX?
- Do the performance of POU units vary for different mixtures of hydrocarbons (BTEX, gasoline, and diesel)?
- Are the fouled POUs susceptible to desorb accumulated contaminants to treated water?

The project objectives are resulting from the following research hypotheses:

Hypothesis I: The certified POU water treatment devices can reduce the BTEX concentration occurring in an accidental spill of mixed petroleum fuels in surface water to concentrations lower than drinking water standards.

Justification of the originality: The performance of POU devices is tested against NSF certified VOC removal claims which are different from BTEX compounds associated with an oil spill. These tests will provide a better assessment of their capacity in realistic spill conditions.

Refutability: The hypothesis will be refuted if the performance of the devices affected when the source of contamination is gasoline or diesel compare to the mixture of pure BTEX.

Hypothesis II: Once their capacity is exceeded, certified POU water treatment devices will continue removing BTEX compounds before starting to desorb progressively.

Justification of the originality: The sensitivity of these devices to their nominal claimed capacity in applications with surface drinking water is important to assess whether these devices can be deployed without concerns about actively managing their capacity.

Refutability**:** The hypothesis will be rejected if devices lose their removal capacity quickly after their claimed capacity is reached and if they desorb compounds.

3.2 Research strategy and methodology

The protocol for evaluating point-of-use drinking water treatment units was designed to simulate real spills of petroleum products into drinking water and verify the removal performance of four types of home filters (two under-the-sink filters, two tap-mounted filters, one refrigerator cartridge, and two pitcher filters). Three tests were carried out to evaluate the BTEX reduction claim of POU devices certified by NSF when the contaminants are: 1) a pure mixture of benzene, toluene, ethylbenzene and three isomers of xylenes, 2) gasoline and 3) diesel fuel.

3.2.1 Experimental setup

3.2.1.1 Chemicals and solutions

The hydrocarbons selected for the assays are the most commonly used fuel in Canada: gasoline and diesel. These mixed fuels have the largest ratio of BTEX amongst other types of hydrocarbons. Gasoline and diesel were collected directly from a local gas station. Moreover, a mixture of pure BTEX was considered as a reagent to compare the real scenarios (spill of petroleum products) with the National Sanitation Foundation (NSF) organic chemical reduction claims. [NSF] Benzene (purity ≥ 99.9%), toluene (purity ≥ 99.8%), ethylbenzene (purity ≥ 99.5%), m-xylene (purity ≥ 99%), p-xylene (purity ≥ 99%), o-xylene (purity ≥ 97%), were purchased from Sigma–Aldrich (St. Louis, Mo). Isotopically labeled internal standard (IS) d6-benzene (purity ≥ 99.0%) and Bromofluorobenzene (purity ≥ 96.0%) were also purchased from Sigma-Aldrich.

Considering the solubilities of benzene, toluene, ethylbenzene and three isomers of xylene (m-, p- and o-), a specified volume of the mentioned contaminants were spiked in a dilution container for mother solution preparation (Assay 1). A bag made of polyvinyl fluoride film, Tedlar$^{®}$ (wall thickness of about 50 µm) with a polypropylene combination valve (on/off and septum) was purchased from Cole-Parmer. The used film in the bag gives an ideal compromise between good chemical properties for VOCs sampling and low cost. Tedlar sample bags are commonly used for air sampling (Beghi & Guillot, 2006). Some EPA methods also recommend Tedlar bags. A 5L Tedlar bag was filled with 4.5 L of ultrapure water prepared daily (18.2 MΩ·cm-1 at 25 °C) with no air bubble. Due to the low solubility of hydrocarbons in water, a magnetic bar was provided in the bag to make partially a homogenous mixture while the solution is injected to the pilot.

The BTEX mother solution concentrations are also chosen to meet the influent concentrations suggested as the challenge concentrations for the POUs in the NSF/ANSI 53 certification standard. These concentrations are obtained by multiplying the USEPA's maximum drinking contaminant level by three. Accordingly, the challenged concentrations used in the assays are selected on the Canadian guidelines.

The BTEX loss in the system is inevitable due to the high evaporation rate of aromatic hydrocarbon and adsorption to the equipment. Hence, some approaches were considered in the apparatus design to minimize BTEX loss, for instance, by reducing air bubbles in the setup, using the plastic tubes certified for hydrocarbons laboratory tests and reducing the length of pipes. To avoid the formation of air bubbles in the bag owing to the degassing during the assay, we filled the bag with ultrapure water 24 h before performing the tests. Thus, before the injection of BTEX, the accumulated air was evacuated. A similar procedure was followed to prepare the gasoline and diesel mother solutions (Assay 2 and 3). Some pretests were conducted to obtain the BTEX concentration in the influent of gasoline and diesel assays close to their concentrations in BTEX assay. Considering the percentage of BTEX in gasoline and diesel, 22.5 w/w% and 12.5 w/w%; respectively, the gasoline and diesel mother solutions were made in the Tedlar bag. Table 3.1 lists the BTEX influent concentrations.

Table 3.1 BTEX influent and mother solution concentrations

Compounds	**Influent limits suggested by NSF (mg/L)**	**Influent limits Canadian guidelines (mg/L)**	**Average influent challenge (mg/L)**	**BTEX mother solution (mg/L)**
Benzene	0.015 ± 30%	0.015 ± 30%	0.045 ± 10%[1]	20 ± 10%
Toluene	3.0 ± 30%	0.4 ± 30%	0.4 ± 10%	177 ± 10%
Ethylbenzene	2.1 ± 30%	0.18 ± 30%	0.18 ± 10%	80 ± 10%
m-xylene	14.4 ± 30%	0.135 ± 30%	0.13 ± 10%	58 ± 10%
o-xylene	8.4 ± 30%	0.075 ± 30%	0.075 ± 10%	34 ± 10%
p-xylene	7.2 ± 30%	0.065 ± 30%	0.065 ± 10%	26 ± 10%
BTEX	35.115 ± 30%	0.870 ± 30%	0.900 ± 10%	397 ± 10%

[1] Benzene concentrations represent nine times than regulated levels in DW (instead of three times) due to its high volatility.

3.2.2 Testing apparatus

The experimental setup should be capable of providing specified flow rates and pressure. Figure 3.2 indicates the experimental setup composed of: (1) centrifugal pump to feed the pilot with tap water from the city of Montreal. (2) An eighty-liter reservoir which supplies a constant overflow and head to prevent pressure variation in the pilot. (3) Air-tight Tedlar bag containing hydrocarbons (BTEX, gasoline, diesel) injected into the system by a peristaltic pump (Figure 3.1). (4) A static mixer right after the injection point to make a homogenous influent going through the POUs. The setup is also equipped with a pressure gage, valves, and flowmeters for three POU units (under-the-sink, tap-mounted or refrigerator cartridge and pitcher) which are tested simultaneously. After the testing of any device was performed (200% of the lifetime), the same type of it manufactured from another company would be displaced. The setup can provide a flow rate of 2 to 8 L/min at a maximum pressure of 50 psi.

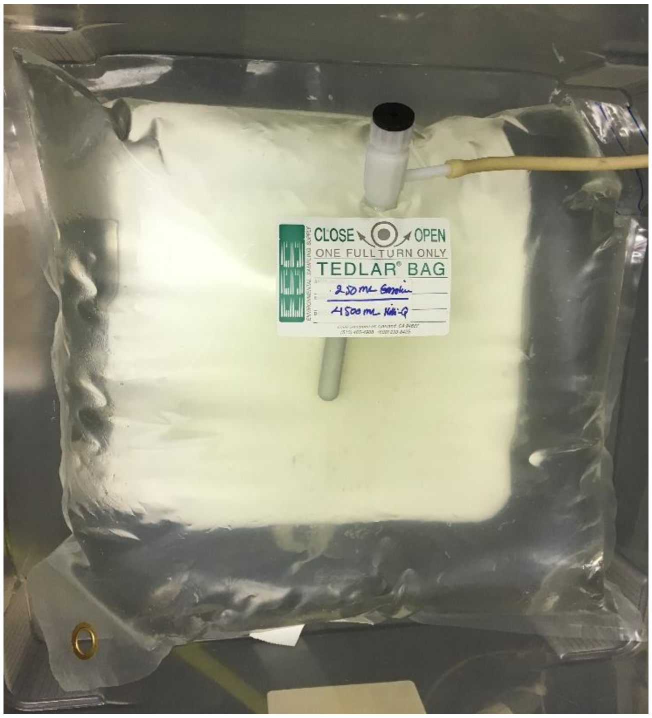


Figure 3.1 Air-tight Tedlar bag containing hydrocarbons (BTEX, gasoline, diesel)

The assays were conducted according to the NSF/ANSI 53-2015 certificated standard for drinking water units in the reduction of organic chemicals. First, the effectiveness of POUs in the removal of a pure mixture of benzene, toluene, ethylbenzene, and xylenes was studied. Then, the experiment was with gasoline and diesel. A total of nine samples were taken for each filter at 0%, 25%, 50%, …175%, 200% of manufacturer's indicated capacity. Initial samples were always collected after a few minutes of flushing as recommended by the manufacturer. The influent and effluent sampling consists of a collection of samples at a very low flow rate, so the sample volume of 1 L was collected in almost one h. Due to the reduction of turbulence and probable BTEX loss, while filling the sampling bottle, the use of composite sampling technique in experiments is required because the influent flowrates of devices are relatively high (2 L/min).

The Point-of-use filter devices manufactured by different manufacturers were bought from local hardware stores. All the POUs were activated carbon-based. One of the under-the-sink units and refrigerator cartridge also included a carbon block (US-CB, RF-CB). The tap-mounted filter was composed of a nonwoven membrane, carbon block and ion exchange (TM-NWM+CB+IX). The other under-the-sink filter was composed of two stages; the first stage was a multi-composed filter and the second one was SBAC as well (US- MCM+PAC). The other tap-mounted filter was composed of granular activated carbon and ion exchange resins (TM-GAC+IX). Two uncertified but popular pour-through POU were also tested, one filter composed of granular activated carbon and ion exchange resin (PT- GAC+IX) and the other was a composition of ion exchange, carbon block and nonwoven membrane (PT- IX+CB+NWM). The characteristics of the POUs announced by the manufacturer are shown in Table 3.2.

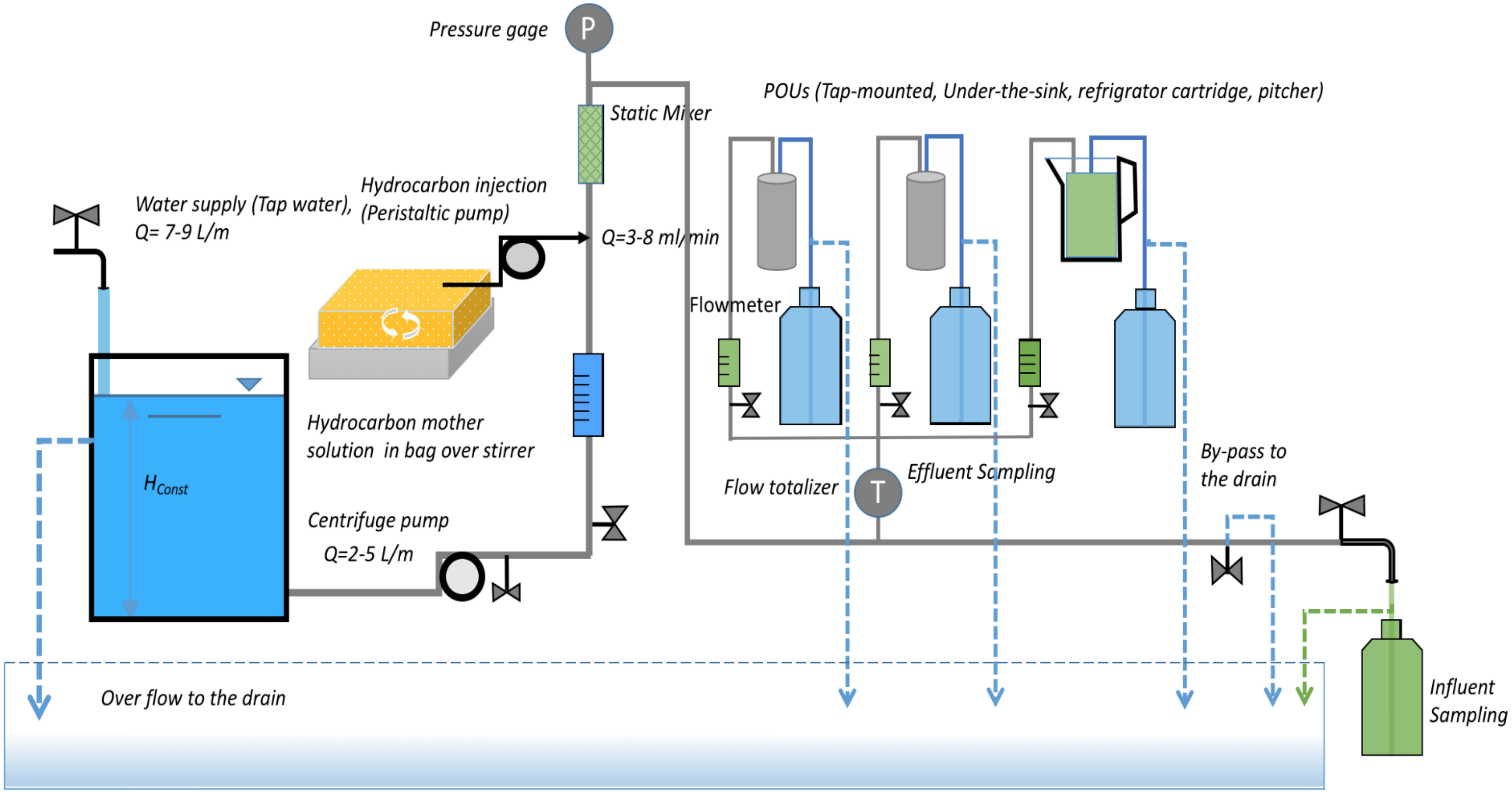


Figure 3.2 Experimental set-up for evaluation of POUs in the removal of diluted hydrocarbon from BTEX and fuel solutions

Table 3.2 Characteristics and operating conditions suggested by manufacturers of the devices; all under-the-sink, tap-mounted and refrigerator POU units are NSF certified for VOC reduction; also both tap-mounted units have NSF certification of individual benzene, toluene and ethylbenzene reduction, and refrigerator cartridge is NSF certified for removal of individual benzene and ethylbenzene, as well. However, pour-through POU units have no NSF certification.

Model	POU ID*	Picture of Device	Materials	Service Flow (LPM)	Pressure Range (psi)	Capacity (L)	Certified by NSF 53 & 42	Claims
Under the Sink	US-CB		Carbon Block	1.9	30-100	1 900	✓	VOC reduction
	US- MCM+PAC		Two stages: Multi composite media + pressed powdered activated carbon	2.3	40-100	2 600	✓	VOC reduction
Tap-mounted	TM-NWM+CB+IX		Two steps: nonwoven membrane + compressed block of carbon and ion exchange zeolite	2.2	20 -100	380	✓	B, T, E, VOC reduction
	TM-GAC+IX		Activated carbon (coconut shells) + Ion exchange	2	20-100	380	✓	B, T, E, VOC reduction
Refrigerator	RF-CB		Extruded carbon block	1.9	30 - 100	760	✓	B, E, VOCs Reduction
Pour-through	PT- IX+CB+NWM		Five stages: Coarse filter screen + Foam distributor + Multi-layer activated carbon & redox alloy+ Ion exchange resin + nonwoven membrane	_	_	150	✓	Hg, Pb, Cr Taste & Odor
	PT- GAC+IX		Granular activated carbon + Ion exchange resin	_	_	150	✓	Cd, Cu, Hg Taste & Odor

3.2.3 Analytical methods

The analysis was performed in the CICEP laboratory for a mixture of BTEX and gasoline assays. Instrumentation issues forced us to resort to a private analytical laboratory (Maxxam Analytics) for the diesel assays. The method was purging extraction and trap without prior filtration and coupled to a GC-MS. The extraction method in the CICEP laboratory was HS-SBSE, and after compounds extraction, they were analyzed by gas chromatography and mass spectrometry techniques.

3.2.3.1 HS-SBSE method

3.2.3.1.1 Extraction procedure and detection

BTEX compounds were extracted from the water samples using a stir bar sorptive extraction (SBSE) method that mimicked the solid phase microextraction (SPME) technique (Arthur, Killam, Buchholz, Pawliszyn, & Berg, 1992; Bicchi, Iori, Rubiolo, & Sandra, 2002). A stir bar coated with polydimethylsiloxane (PDMS) has been commercialized under the name of Twister, was used as the SPME fiber to trap BTEX in the gas phase of the vial. The extraction is performed by placing a 50 mL sample or diluted one in a headspace vial. The coated stir bars were attached to the back of the screw cap in the headspace of the sample with the help of a magnet, and the sample was extracted using a stir bar for 60 minutes with the speed of 1250 rpm.

The on-line desorption system installed on the GC-MS was a Thermal Desorption Unit (TDU) and a Cooled Injection System (CIS) provided by Gerstel Inc (Baltimore, MD). After the extraction, the stir bars were inserted in a glass thermal desorption tube and thermally desorbed at 280 °C in the TDU. The TDU is connected directly to the CIS, which serves both as a cryo-focusing trap (-150 °C) and as a gas chromatography (GC) inlet. The trapped BTEX were then transferred through the GC column by helium gas (1.5 mL/min) to the mass spectrometer (MS) from Varian (Pablo Alto, CA) to be ionized and measured at different retention times. HS–SBSE-GC/MS method was used for the analysis of benzene, toluene, ethylbenzene, and xylenes for BTEX and gasoline assays (Golby & Stubbs, 2003).

3.2.3.1.2 Validation

The performance of the analytical method was assessed by Province of Québec’s Ministry of the Environment guideline based on the validation protocol for environmental chemistry analysis. A mix of deuterated d_6-benzene and bromofluorobenzene was used to correct the signal from sample losses due to incomplete extraction. The internal standard solution (1 000 ng/L) was added to the sample before the extraction step. Thus, concentrations of BTEX residues were calculated using the ratio of target compounds area to that of the IS. The internal standard solution (stock solution) was prepared at a concentration of 1 000 µg/L and was usually prepared fortnightly. Meta and para-xylene could not be enough separated by a chromatographic column. Thus, they were combined and analyzed as the sum of corresponding peak areas because of the same fragmentation patterns.

The linearity, limits of detection, accuracy, and inter and intraday precision of the method were calculated to validate the analytical method (Table 3.3). The linearity of the method was determined by analyzing spiked tap water samples in the range of 10 ng/L to 5 000 ng/L. A seven-point calibration curve (blank included) was obtained by spiking tap water at 50, 100, 250, 500, 1 000, 2 500 ng/L. The linear range experiments provided the necessary information to estimate the limit of detections (LOD) and the limit of quantification (LOQ). The LOD and LOQ were determined as 3 and ten times, the standard deviation of the y-intercept divided by the slope of the calibration curve in a tap water sample. Relative error (RE%) and relative standard deviation (RSD%) define the accuracy values of the analytical method. All relative standard deviations calculated for duplicate analyses of each sample were less than 15%. The relative errors of the same spiked samples at two different concentrations (100 and 1 000 ng/L) determined the accuracy value of the extraction method. The errors in all extractions were less than 20%. The inter and intraday precision were estimated by analyzing six replicates at two quality control (QC) levels, 100 ng/L and 1 000 ng/L. The intraday precision of the tests was estimated by calculating the relative standard deviation for the analysis of the six replicates QC samples. Six replicates quality control samples on three consecutive days were analyzed to determine the intraday precision. The accuracy was calculated based on the given formula (mean found concentration per taken concentration) ×100.

Table 3.3 Limit of detection of BTEX in water by HS–SBSE-GC–MS

Compounds	**r^2**	**LOD (ng/L)**	**Intraday precision (%)**		**Interday precision (%)**	
			100	**1 000**	**100**	**1 000**
Benzene	0.998	60	11	7	3	8
Toluene	0.999	47	8	6	8	3
Ethylbenzene	0.998	41	10	13	7	7
m/p-Xylene	0.999	48	9	13	2	4
o-Xylene	0.999	44	5	12	4	2

3.2.3.2 Purge and trap-GC/MS method

After collecting the composite samples in one-liter bottles for diesel assays, samples were transferred without headspace to the duplicated 40±2 mL vials containing 2 g of sodium thiosulfate as the preservative. Samples stored cool (<10° C) from the time of collection until they were delivered to the laboratory. Two methods were performed for validation of analysis. In order to validate instrumental readings, a pure lab water to which all digestion chemicals are added and then digested with samples, should show below detection limit results for each analyte (Method Blank) and another method blank that has had a known concentration of the analytes of target added to it then digested with samples (Laboratory Fortified Blank (LFB). Recovery value represents the percentage of instrumental reading per true value, which should be close to 100%. Table 3.4 shows the reported limit of detection and validation results of quality assurance and quality control provided by the Maxxam laboratory for analyzing BTEX for diesel assays.

Table 3.4 Reported limit of detection (μg/L) and validation results (% recovery and method blank values) by Maxxam laboratory for analyzing BTEX for diesel assay

Compounds	**Limit of detection (LOD reported)** (ng/L)	**Validation**	
		LFB (% Recovery)	**Method blank** (μg/L)
Benzene	200	103	<0.2
Toluene	100	109	<0.1
Ethylbenzene	100	104	<0.1
Xylene	400	104	<0.4

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Experimental design

This chapter presents the results of the laboratory testing on hydrocarbon removal by seven POU devices including four types (Under-the-sink, tap-mounted, refrigerator, and pour-through). Table 4.1 summarizes the experimental design. Three types of hydrocarbon mixtures were tested, including a mix of BTEX, gasoline, and diesel to provide a wide range of fuel to consider the diverse types of accidental spills that could occur and be transported to drinking water sources. The assays of each point-of-use device were conducted for a period ranging from 6 to 42 hours. The testing duration was adjusted as a function of the operating lifetime and the flow rate recommended by the manufacturer of the POU units.

Moreover, the physicochemical characteristics of the contaminants affect the flow rate. The concentrations of fuels injected into the pilot were prepared of a 2 mL mixture of benzene, toluene, ethylbenzene and xylenes, 200 mL gasoline and 300 mL diesel in 4.5 L of ultrapure water in the sealed Tedlar bag for each assay (Table 4.1). These solutions were prepared for the everyday pilot run. The selection of these ratios was derived from the influent challenge concentrations recommended in ANSI/NSF Standard 53 and the percentage of total BTEX in gasoline and diesel. In terms of types and the number of POUs tested in parallel, the total flow rate entering the setup was determined. The flow rate to each unit reduces as the device approaches its end of life. With the help of a bypass valve, the total flow rate and dilution factor were kept constant during the pilot run to maintain the same influent concentrations. A total of nine samples were taken for each point-of-use filter from the onset of the experiment up to 200% of the manufacturer's indicated capacity. Also, at least two composite samples of the influent entering the POUs were collected every 3 hours. The significant standard deviation between the repeated samples collected at the beginning and end of the testing period (per each run) could be due to the heterogeneity of the injecting solution, volatility of the BTEX compounds, adsorption, and desorption characteristics of fuel in the pilot, fluctuation of pressure and flow and evaporation of compounds while sampling.

The largest experimental challenge of this project was dealing with the variability in the influent concentrations and the losses by volatilization and heterogeneity of the mixtures. Thus, composite sampling was provided. It provides some buffering to the variability in influent concentrations in the feed solutions. The analysis was performed in the CICEP laboratory for BTEX and gasoline assays, after the instrument failure, it was completed by Maxxam laboratory.

Table 4.1 Experimental design for testing the mixtures of BTEX, gasoline and diesel removal by 7 POUs with different technologies and removal capacities

Assay	**POU ID**	**Test duration (h)**	**Bag Concentration (v/v%)**	**Total Flow (L/min)**	**Influent Concentration of total BTEX (mean ± SD) (μg/L)**	**Number of Samples**		**Analyzed by**
						Inf	**Eff**	
BTEX Assay	US-CB	34	0.045%	2.0±1.0	359±168	10	9	CICEP
	US-MCM+PAC	40			353±188	11	9	
	TM-NWM+CB+IX	6			815±205	4	9	
	TM-GAC+IX	7			610±65	4	9	
	RF-CB	13			1 130±101	4	9	
	PT-IX+CB+NWM	20			1 201±104	6	9	
	PT- GAC + IX	14			375±167	4	9	
Gasoline Assay	US-CB	37	4.50%	3.0±1.5	584±72	5	9	CICEP
	US-MCM+PAC	42			1 134±435	7	9	
	TM-NWM+CB+IX	6			1856±70	2	9	
	TM-GAC+IX	7			640±50	2	9	
	RF-CB	8			1 264±242	2	9	
	PT-IX+CB+NWM	20			1 134±435	6	9	
	PT- GAC + IX	14			553±80	5	9	
Diesel Assay	US-CB	37	6.70%	4.0±1.0	320±275	11	9	Maxxam
	US-MCM+PAC	42			340±237	3	3	
	TM-NWM+CB+IX	6			340±205	3	9	
	TM-GAC+IX	7			727±90	2	9	
	RF-CB	8			106±35	2	9	
	PT-IX+CB+NWM	20			123±34	8	9	
	PT-GAC+IX	14			390±290	4	9	

4.2 BTEX assay

4.2.1 Performance of pour-through units for BTEX removal

The overall performance of pour-through POU for the removal of individual compounds of BTEX and total BTEX, for a BTEX mixture diluted in tap water, is presented in Figure 4.1 . When appropriate, reference lines to standards or guideline values are shown by dashed lines.

As stated by the manufacturer of the pour-through filters, PT-IX+CB+NWM is composed of five stages. First, the water passes through a coarse filter screen to reduce suspended solids; the second stage is made of foam distributor then the water flows through multi-layer activated carbon and oxidation reduction alloy to remove organic contaminants. The fourth stage is dual comprehensive ion exchange for the reduction of inorganic compounds, and at last the remaining suspended solids will be removed by ultrafine screen non-woven membrane layers. PT-GAC-IX is a mixture composed of granular activated carbon and ion exchange.

For high influent mean concentrations of total BTEX for PT-GAC-IX and PT-IX+CB+NWM (375±167 µg/L and 1 201±104 µg/L), the effluent BTEX concentrations were 90±15 µg/L and 200±100 µg/L, respectively. The pour-through POUs are not NSF certified for VOCs reduction. Even with an influent (375±167 µg/L) close to the target influent concentration (295 µg BTEX/L), the pour-through does not remove 100% of the BTEX, as a concentration of 90±15 µg/L of total BTEX was detected in the effluent. Although this effluent concentration is less than the Canadian guideline for the total BTEX, the concentrations of the individual compounds of BTEX concentrations should be considered. For instance, the mean benzene concentration in the filtered water by PT-GAC-IX was 1.9±0.4 µg/L. Although the mean benzene concentration was less than Canadian guideline (5 µg/L), this concentration does not meet the Quebec drinking water standard (0.5 µg/L). Moreover, while the concentration of ethylbenzene (18±4 µg/L) was less than Canadian guideline (140 µg/L), it was noticeably higher than the odor threshold (1.6 µg/L). Toluene and xylenes concentrations were also more than Canadian odor guidelines. Consequently, the performance would decline when the influent concentration increases (1 201±104 µg/L) and approaches the influent challenge concentration (900±90 µg/L). The effluent concentration nearly doubled (200±100 µg/L) when the influent increased 3-fold.

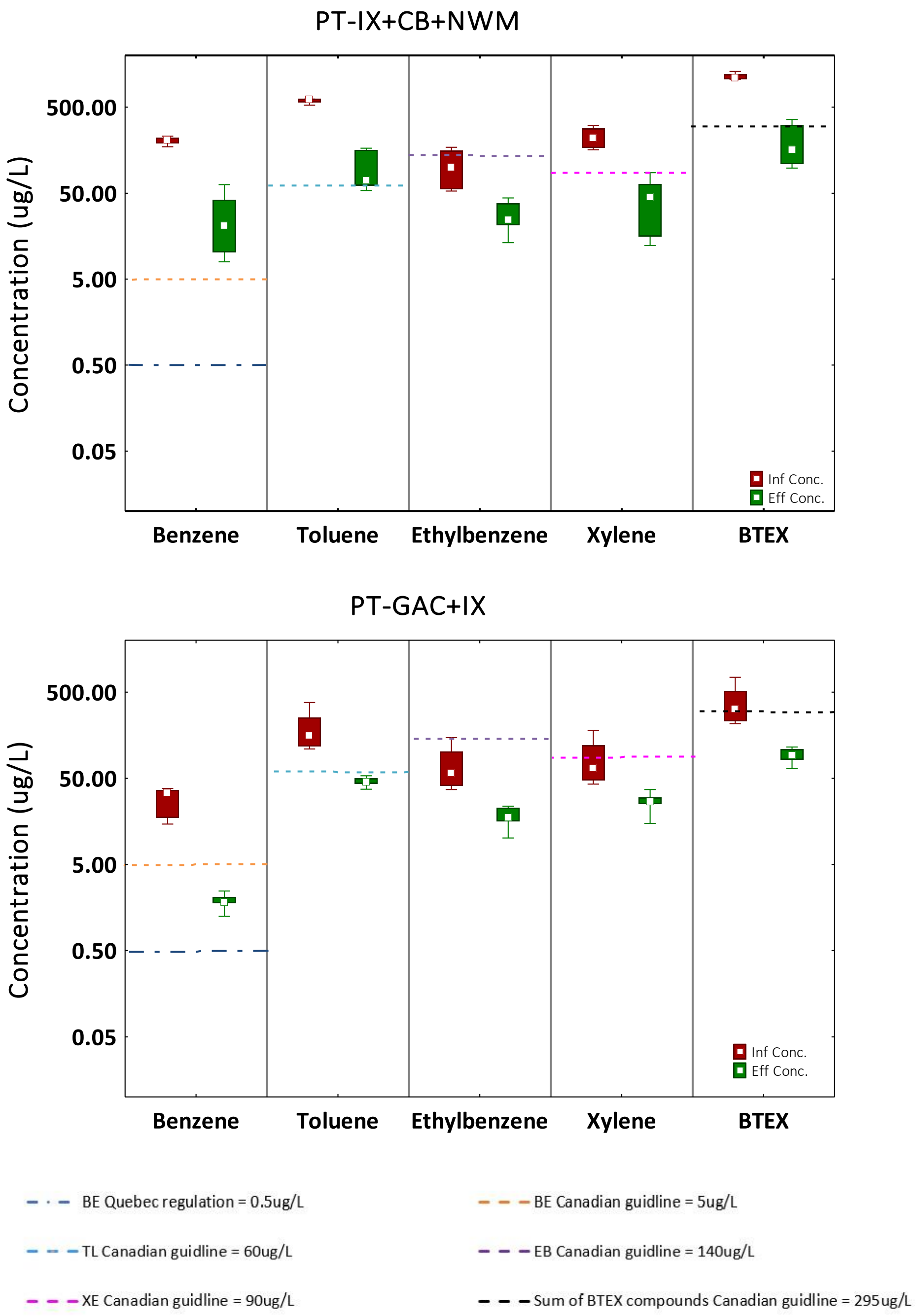


Figure 4.1 BTEX removal performance of pour-through filters (TM-NWM+CB+IX and TM-GAC+IX) for a mix of BTEX diluted in tap water with the mean influent concentration of 375±167 µg/L and 1 201±104 µg/L. Dashed lines show reference standard and guideline concentrations. 50% of the limit of detections for each compound is considered for non-detected values. Boxes represent 25th-75th percentiles, whiskers min-max values, and the square shows median concentrations.

4.2.2 Performance of refrigerator cartridge for BTEX removal

The influent and effluent mean concentrations of total BTEX for RF-CB were 1 130±101 µg/L and 0.56±0.25 µg/L (Figure 4.2). This device is NSF certified for the removal of VOCs, benzene, and ethylbenzene. As expected, the refrigerator cartridge effectively removes BTEX. Although the influent concentration for the total BTEX was four times more than Canadian guideline (1 130±101 µg/L), no trace of benzene, toluene, and ethylbenzene was detected in the effluent. The mean xylenes concentration in the filtered water was 0.24±0.08 µg/L, a concentration well below the acceptable concentration established for total xylenes by Health Canada.

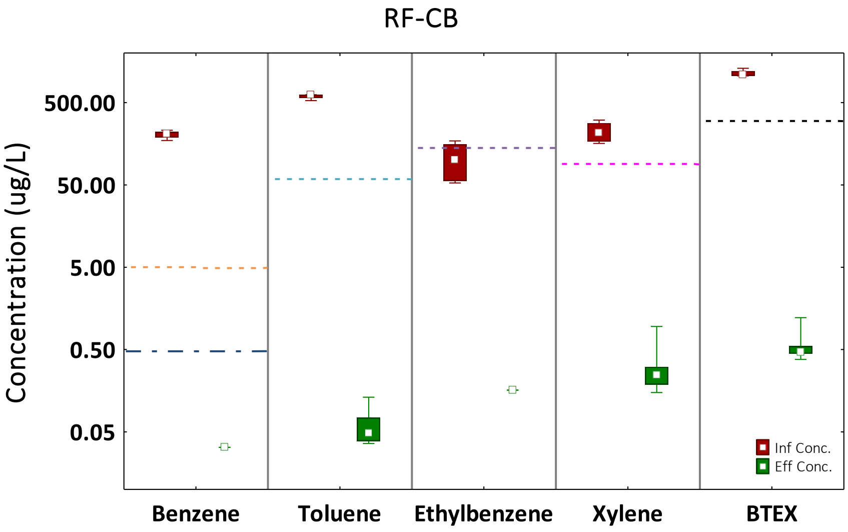


Figure 4.2 BTEX removal performance of refrigerator POU unit for a BTEX mixture diluted in tap water with the mean influent concentration of 1 130±101 µg/L. Dashed lines show reference standard and guideline concentrations. 50% of the limit of detections for each compound is considered for non-detected values. Boxes represent 25th-75th percentiles, whiskers min-max values, and the square shows median concentrations.

4.2.3 Performance of tap-mounted point-of-use devices for BTEX removal

An overview of the efficiency of tap-mounted POU units for the reduction of benzene, toluene, ethylbenzene, and xylenes, and the total BTEX, for a mix of BTEX diluted in tap water, is shown in Figure 4.3.

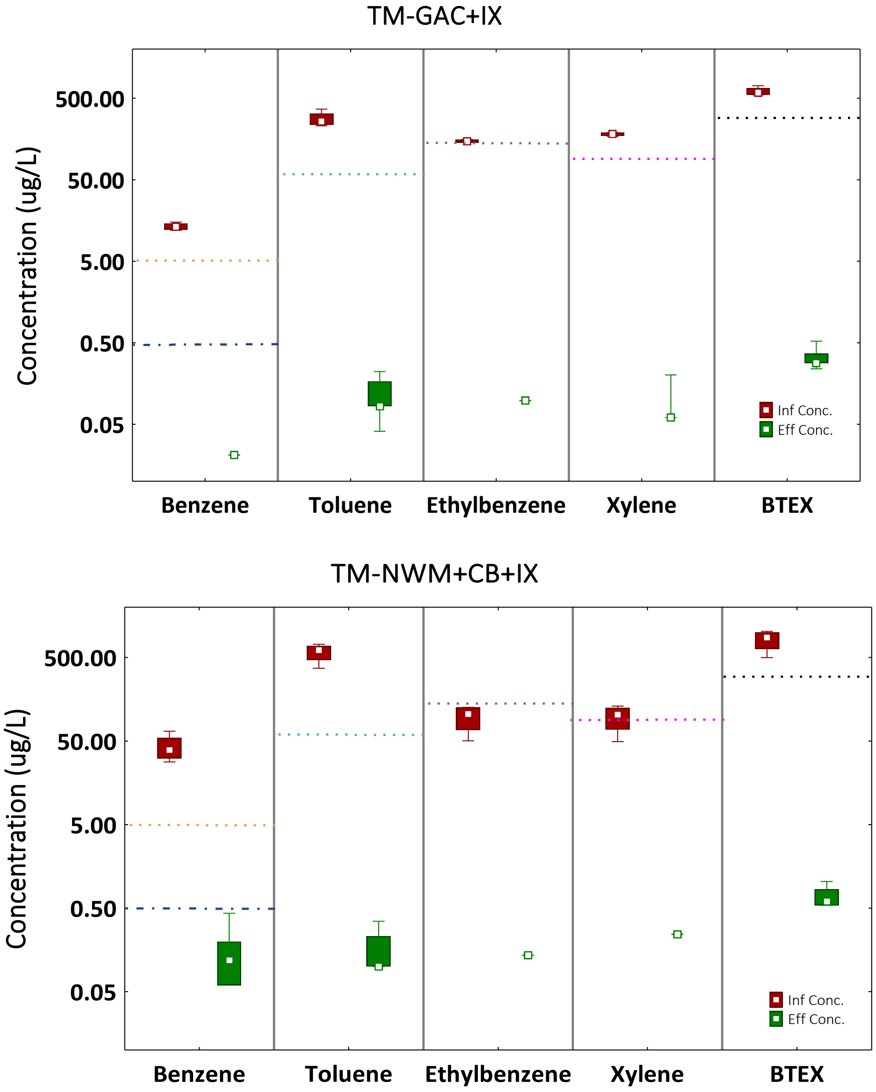


Figure 4.3 BTEX removal performance of tap-mounted filters (TM-NWM+CB+IX and TM-GAC+IX) for a mix of BTEX diluted in tap water with mean influent concentrations of 815±205 µg/L and 610±65 µg/L. Dashed lines show reference standard and guideline concentrations. 50% of the limit of detections for each compound is considered for non-detected values. Boxes represent 25th-75th percentiles, whiskers min-max values, and the square shows median concentrations.

According to the manufacturer of the POUs, the unit TM-NWM+CB+IX is composed of a two-step process. First, water cross through a non-woven membrane around the filter to trap sediment and particles. Then, the water passes through a compressed block of activated carbon and zeolites. The materials used in TM-GAC+IX filter are grains of activated carbon made of coconut shell and ion exchange resins. The influent mean concentrations of total BTEX for evaluating the performance of TM-NWM+CB+IX and TM-GAC+IX point-of-use devices were 815±205 µg/L and 610±65 µg/L.

The effluent concentrations of total BTEX for TM-NWM+CB+IX and TM-GAC+IX POU units were 0.7± 0.18 µg/L and 0.36±0.1 µg/L, respectively. Both tap-mounted point-of-use units are NSF certified for the removal of VOCs, benzene, toluene, and ethylbenzene, and almost identical results have obtained. Except for benzene and toluene in two samples, no trace of toluene, ethylbenzene, and xylenes are observed in the effluents of TM-NWM+CB+IX unit from 0 to 200% of the operating lifetime of both devices.

4.2.4 Performance of under-the-sink point-of-use devices for BTEX removal

An overview of the removal efficiency of under-the-sink POU units for the removal of benzene, toluene, ethylbenzene, and xylenes, as well as the total for a mixture of BTEX diluted in tap water, are depicted in Figure 4.4. According to the manufacturer of the POU devices, US-MCM+PAC is composed of a dual-stage carbon filtration system on multi-composite media and solid pressed-carbon block. The material used in US-CB filter is a carbon block; the manufacturer does not mention the detail of the technology used in the filter.

The influent mean concentrations of total BTEX for evaluating the performance of US-MCM+PAC and US-CB point-of-use devices were 353±188 µg/L and 315±182 µg/L. Except for a low toluene concentration, no BTEX was detected in the effluent of under-the-sink filters. Results are coherent with the proven NSF certification claims of these point-of-use devices for VOCs reduction.

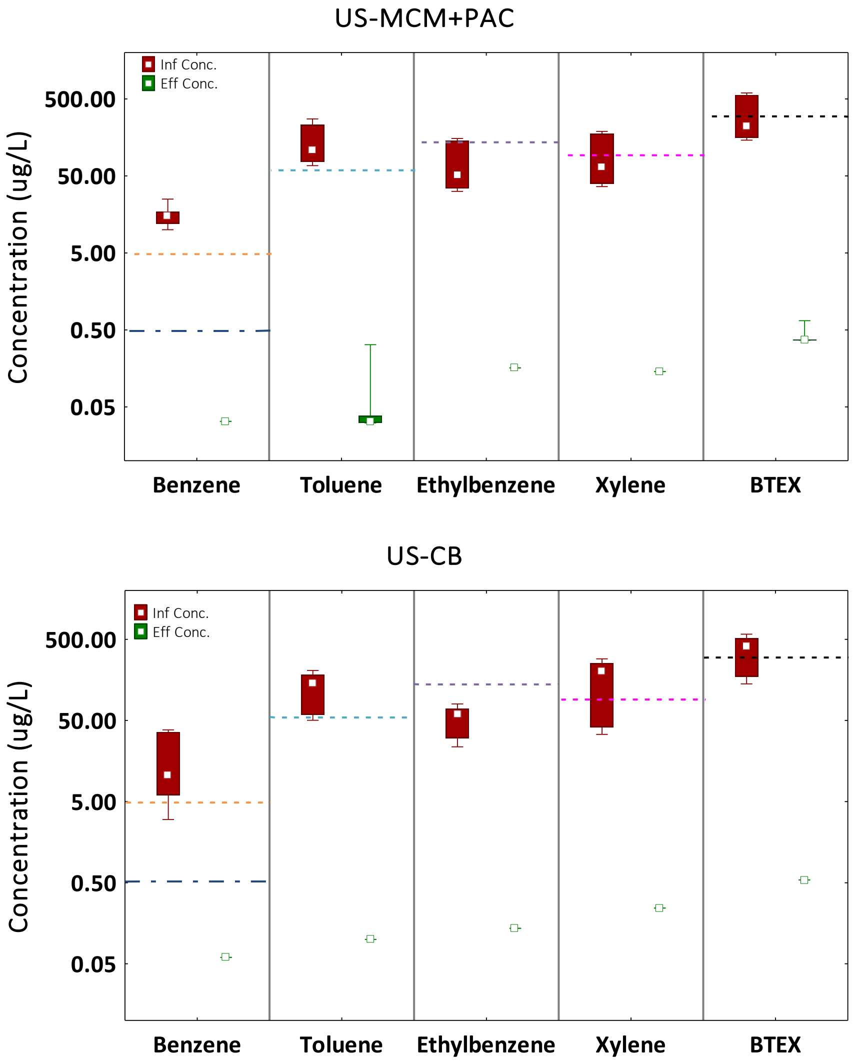


Figure 4.4 BTEX removal performance of under-the-sink filters (US-MCM+PAC and US-CB) for BTEX mixture diluted in tap water with mean influent concentrations of 353±188 µg/L and 315±182 µg/L. Dashed lines show reference standard and guideline concentrations. 50% of the limit of detections for each compound is considered for non-detected values. Boxes represent 25th-75th percentiles, whiskers min-max values, and the square shows median concentrations.

4.3 Gasoline and diesel assays

4.3.1 Performance of pour-through point-of-use devices for BTEX removal

Figure 4.5 presents an overview efficiency of two pour-through POU units for the removal of target compounds when the spill of gasoline and diesel in drinking water sources is simulated.

The influent mean concentrations of total BTEX for evaluating the performance of PT-GAC-IX and PT-IX+CB+NWM point-of-use devices were 553±73 µg/L and 1134±435 µg/L for gasoline assay, and 390±290 µg/L and 123±34 µg/L in diesel assay. Corresponding effluent concentrations of total BTEX for PT-GAC-IX and PT-IX+CB+NWM POU units were 82±17 µg/L and 296±164 µg/L in gasoline assay and 24±25 µg/L and 35±34 µg/L in diesel assay (Figure 4.5).

The pour-through POU devices do not have NSF certification for VOCs reduction. We tested a wide range of influent concentrations, from low values 123±34 µg/L, even below the summation of BTEX guideline values (295 µg/L), to higher concentrations of 1 134±435 µg/L. Benzene was poorly removed by these two devices, with concentrations in the effluent often exceeding the Quebec standard of 0.5 µg/L by more than an order of magnitude. For toluene, effluent concentrations did not meet the odor threshold. Overall, the pour-through units were not able to remove the other BTEX compounds below our detection limits, and the performance of devices was proportional to the feed concentration. The more influent BTEX concentration enters the pour-through unit, the more BTEX is detected in the effluent.

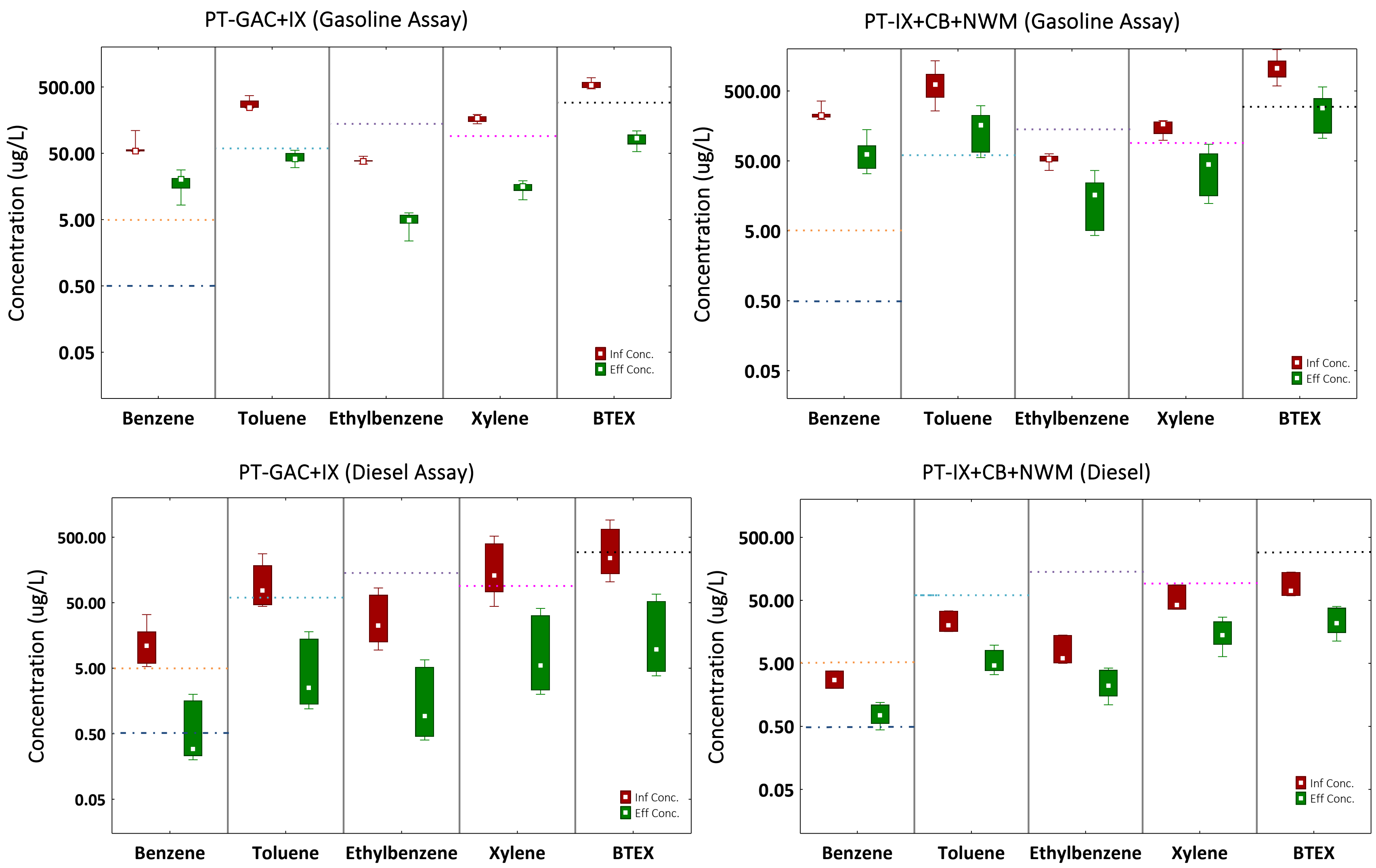


Figure 4.5 BTEX removal performance of pour-through POUs (PT-GAC-IX and PT-IX+CB+NWM) for gasoline and diesel diluted in tap water with mean influent concentrations of 553±73 µg/L and 1 134±435 µg/L. Dashed lines show reference standard and guideline concentrations. 50% of the limit of detections for each compound is considered for non-detected values. Boxes represent 25th-75th percentiles, whiskers min-max values, and the square shows median concentrations.

4.3.2 Performance of refrigerator point-of-use devices for BTEX removal

The overall BTEX removal performance and individual compounds of BTEX of refrigerator filter (RF-CB) for gasoline and diesel diluted in tap water, is presented in Figure 4.6.

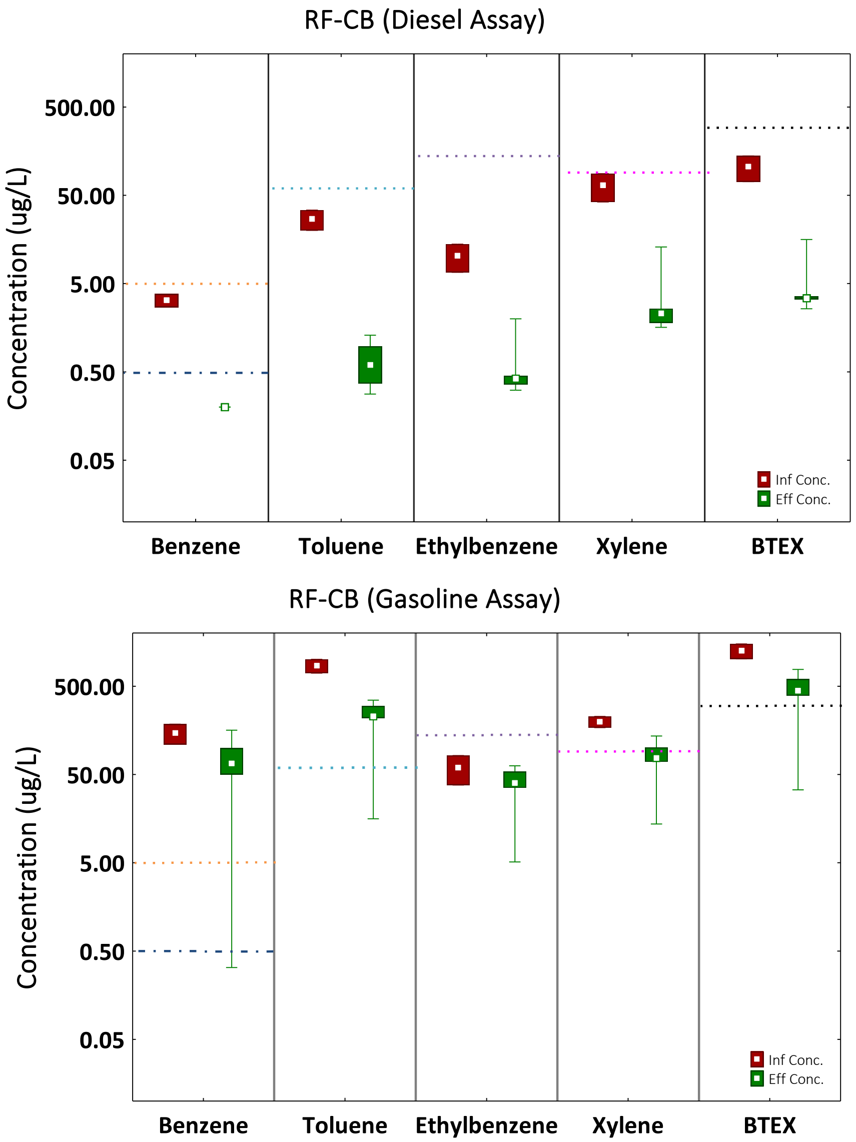


Figure 4.6 BTEX removal performance of refrigerator POU (RF-CB) for gasoline and diesel diluted in tap water with mean influent concentrations of 1 264±242 µg/L and 106±35 µg/L. Dashed lines show reference standard and guideline concentrations. 50% of the limit of detections for each compound is considered for non-detected values. Boxes represent 25th-75th percentiles, whiskers min-max values, and the square shows median concentrations.

According to the manufacturer prescribed operating condition of this filter, the assays completed in 8 hours and two influent samples were collected in test duration. Consequently, in Figure 4.6 no whisker is observed in influent concentrations. The influent mean concentrations of total BTEX in gasoline and diesel assays are 1 264±242 µg/L and 106±35 µg/L, which are reduced to 427±171 µg/L and 5±4 µg/L in effluents by refrigerator cartridge. Although the refrigerator cartridge is NSF certified for the reduction of VOCs, benzene, and ethylbenzene, its performance reflected influent concentration. Concentrations in the feed were comparable to those in the pure BTEX assay (Figure 4.2) and the gasoline assay (Figure 4.6). However, removals are much reduced when gasoline was used, as shown by the partial or complete breakthrough for all compounds tested. In the case of diesel, for which the influent BTEX concentrations were much lower, improved removals are seen but still lower than for BTEX in water removals.

4.3.3 Performance of tap-mounted point-of-use devices for BTEX removal

Influent and effluent each compound of BTEX and total BTEX for evaluation of the two tap-mounted point-of-use units in gasoline and diesel assays are depicted in Figure 4.7. The influent mean concentrations of total BTEX for assessing the performance of TM-NWM+CB+IX and TM-GAC+IX point-of-use devices were 1 856±70 µg/L and 640±50 µg/L in gasoline assay while they were 340±205 µg/L and 727±90 µg/L in the diesel assay. Corresponding effluent concentrations of total BTEX for TM-NWM+CB+IX and TM-GAC+IX POU units were 131±37 µg/L and 111±56 µg/L in gasoline assay and 88±65 µg/L and 92±50 µg/L in diesel assay. Although both tap-mounted point-of-use units are certified for the reduction of VOCs, benzene, toluene, and ethylbenzene individually by NSF 53, their performance for removal of BTEX from gasoline and diesel was not as good as BTEX assay. Again, it indicates that gasoline and diesel as the source of contamination affect the removal efficiency.

In the diesel assay, except for xylenes, other compounds of BTEX were below Canadian guideline in both faucet-mounted POU units. However, benzene concentrations did not meet Québec drinking water standard (0.5 µg/L), and the concentrations of ethylbenzene were detected exceeded by 2 to 10 times the odor threshold (1.6 µg/L).

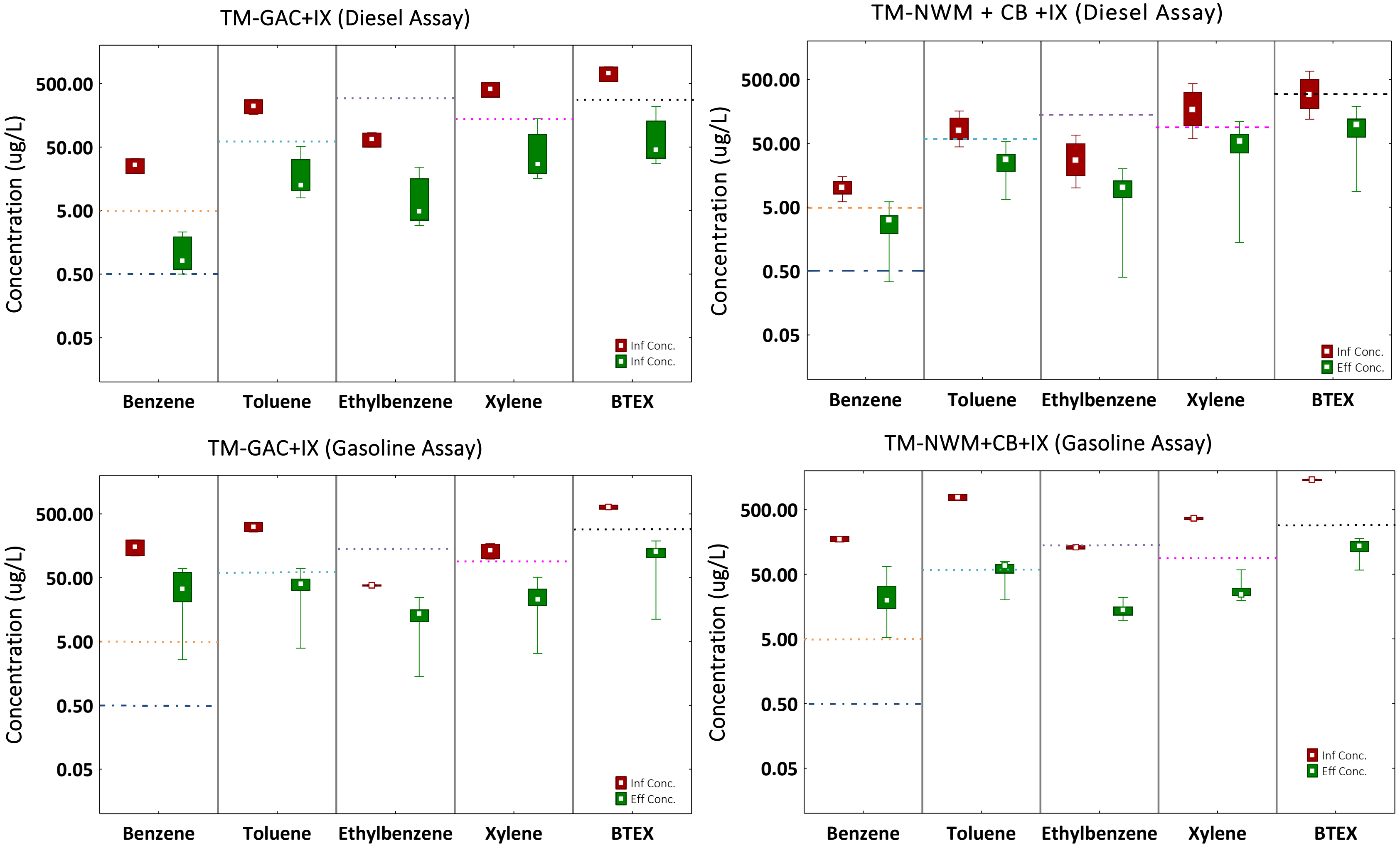


Figure 4.7 BTEX removal performance of tap-mounted filters (TM-NWS + CB + IX and TM-GAC+IX) for gasoline and diesel diluted in tap water with mean influent concentrations are 1 856±70 µg/L and 640±50 µg/L in gasoline assay and 340±205 µg/L and 727±90 µg/L in diesel assay. Dashed lines show reference standard and guideline concentrations. 50% of the limit of detections for each compound is considered for non-detected values. Boxes represent 25th-75th percentiles, whiskers min-max values, and the square shows median concentrations.

4.3.4 Performance of under-the-sink point-of-use devices for BTEX removal

Figure 4.8 illustrates an overview of the efficiency of under-the-sink POU units for the reduction of benzene, toluene, ethylbenzene, and xylenes, the total BTEX as well for diluted gasoline and diesel in tap water. The influent and effluent mean concentrations of total BTEX for evaluating the performance of US-CB filter, were 584±72 µg/L and 13±22 µg/L in gasoline assay while the influent and effluent BTEX mean concentration in assessing the efficiency of US-MCM+PAC unit were 1 134±435 µg/L and 130± 275 µg/L, in gasoline assay.

The results for US-CB point-of-use unit show that concentrations of toluene, ethylbenzene, and xylenes remained below the Canadian guideline values up to 200% operating lifetime of this point-of-use. However, toluene and ethylbenzene concentrations exceed the odor threshold. If the Quebec drinking water standard of 0.5 µg/L benzene is considered, this device can only be used up to 50% of its capacity. The effluent BTEX concentration of the US-MCM+PAC device in gasoline assay is ten times more than US-CB point-of-use effluent concentration. It shows that the US-MCM+PAC has a superior capacity as compared to the US-CB device.

The performance for BTEX removal of the US-CB device decreases when exposed to diesel as compared to gasoline. With an influent mean concentration of 320±272 µg/L, this device could not reduce the total BTEX concentrations to less than 197±175 µg/L. No exceedance of Canadian health and odor guidelines is observed in the removal of toluene. However, the ethylbenzene concentration exceeds the odor threshold in all samples. In the diesel assay, the US-MCM+PAC point-of-use was not able to reach 200% of its capacity and clogged at 50% of its operating lifetime. The influent BTEX concentration was 340±237 µg/L in the first eight hours of its usage. For this reason, the whiskers are not observed in the graph.

Overall, we observe a lower BTEX removal capacity when the US-MCM+PAC and US-CB units are exposed to gasoline and diesel, rather than BTEX in water.

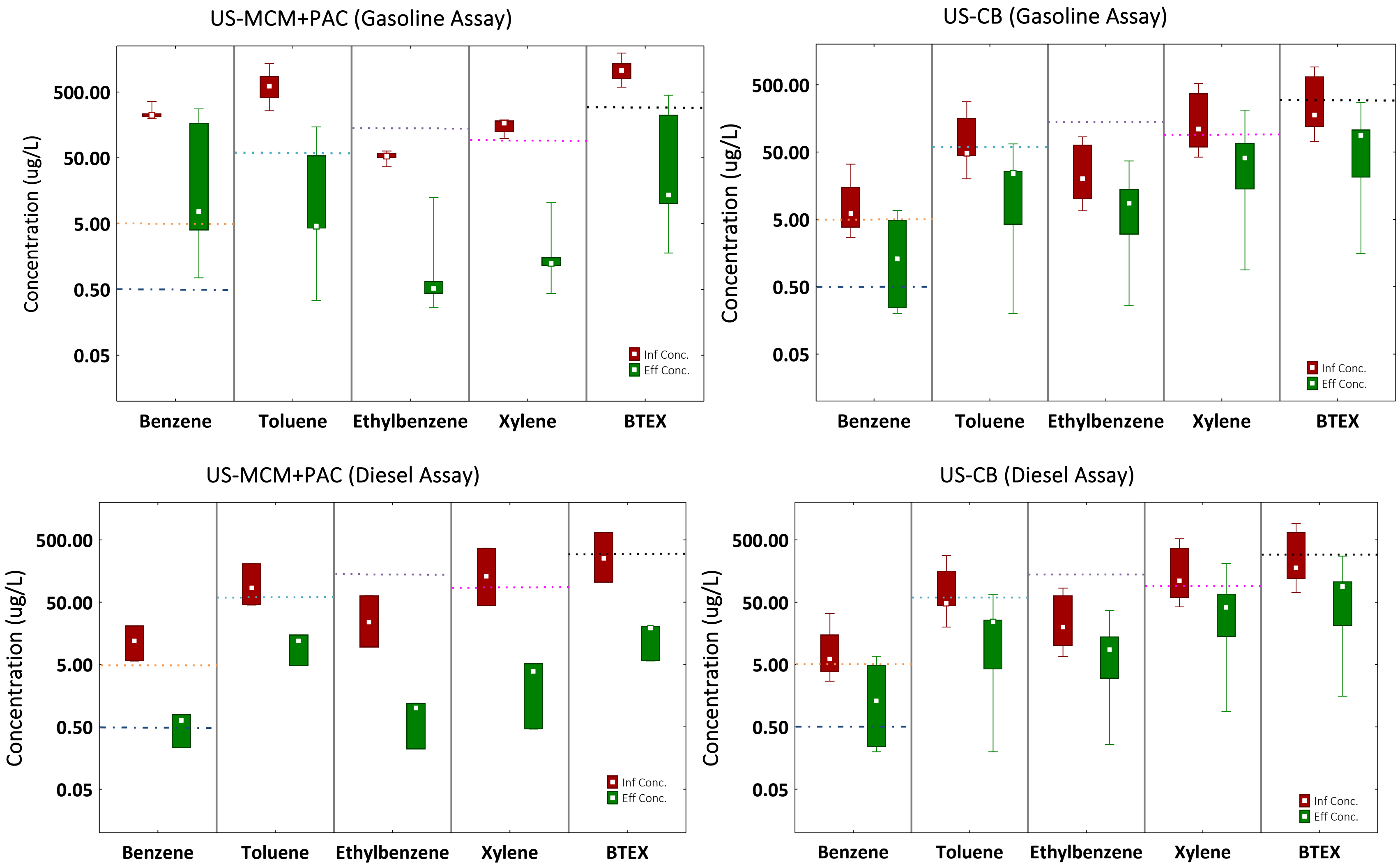


Figure 4.8 BTEX removal performance of under-the-sink POU (US-MCM+PAC and US-CB) for gasoline diluted in tap water with mean influent concentrations of 1 134±435 µg/L and 584±72 µg/L, and for diesel assays are 320±275 µg/L and 340±237 µg/L. Dashed lines show reference standard and guideline concentrations. 50% of the limit of detections for each compound is considered for non-detected values. Boxes represent 25th-75th percentiles, whiskers min-max values, and the square shows median concentrations.

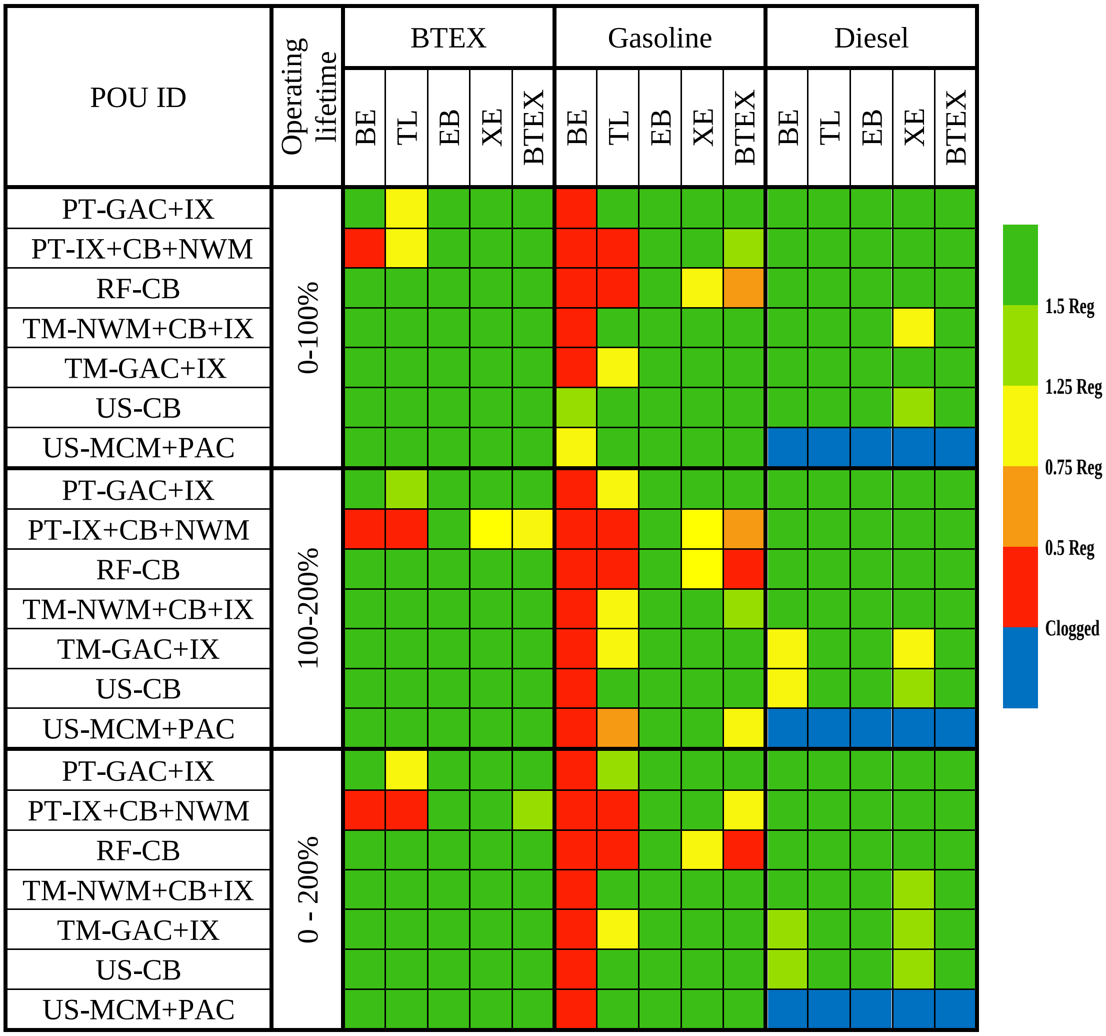
4.4 Evaluation of POU units for BTEX removal

For the sake of simplicity, results are summarized in two heat map graphs based on the: 1) the effluent concentrations comparing concentrations to the regulated health-based standards (Figure 4.9), and 2) the removal efficiency of point-of-use for the tested hydrocarbons (Figure 4.10).

4.4.1 Assessment of BTEX effluent concentrations of tested POUs

As shown in Figure 4.9, the heat map of the effluent mean concentrations of the four target compounds for the three tested mixtures of compounds (BTEX, gasoline, and diesel) achieved over 0 to 100% and 100% to 200% of the operating lifetime for each device. Overall, the heat map demonstrates the concentrations which exceed the thresholds. As shown in Table 4.2, the heat map of effluent concentrations is made in reference to 0.50 to 1.50 of the Canadian guidelines of BTEX. For the gasoline assays, it must be noted that the BTEX influent concentrations were higher compared to the other two assays. Accordingly, most of the effluent concentrations exceeded the guideline are observed. As shown in the heat map, benzene breaks through right away from the beginning of the usage of all tested POUs (except the under-the-sink composed of carbon block (US-CB). This preferential breakthrough reflects the fact that because it is the most water-soluble compounds among other BTEX and that it presents at a higher percentage in gasoline. The breakthrough of the US-CB POU device occurred close to the end of operating lifetime, albeit the effluent benzene concentration does not meet the Quebec drinking water standard for more than half of the lifetime. Besides benzene, the other red cells are found for toluene which is the second most water-soluble compound of total BTEX. Accordingly, the PT-IX+CB+NWM, RF-CB and TM-GAC+IX devices were not effective for the removal of toluene.

The influent concentration of benzene and toluene in the BTEX assay were high (BE=204±20 µg/L, TL=600±42 µg/L). They exceeded the capacity of the PT-IX+CB+NWM POU, as this device failed to reduce benzene concentration to low levels, right at the beginning of the usage. The performance of this device in the removal of toluene declines even more after 150% of the operating lifetime, although the mean effluent concentrations during the lifetime were close to the guideline (66±12 µg/L). When considering diesel as the source of BTEX, it should be noted that the influent mean BTEX concentrations were much lower as compared to those during the gasoline and BTEX assay. In that case, all tested POU units were able to reduce BTEX concentrations below the Canadian guideline values, except one of the tap-mounted made of carbon block and resin, which was not certified in xylenes removal. The under-the-sink POUs were not effective in the complete removal (below LOD) of benzene and xylenes during 100 - 200% of their lifetime.



POU ID	Operating lifetime	BTEX					Gasoline					Diesel				
		BE	TL	EB	XE	BTEX	BE	TL	EB	XE	BTEX	BE	TL	EB	XE	BTEX
PT-GAC+IX	0-100%	🟩	🟨	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
PT-IX+CB+NWM		🟥	🟨	🟩	🟩	🟩	🟥	🟥	🟩	🟩	🟢	🟩	🟩	🟩	🟩	🟩
RF-CB		🟩	🟩	🟩	🟩	🟩	🟥	🟥	🟩	🟨	🟧	🟩	🟩	🟩	🟩	🟩
TM-NWM+CB+IX		🟩	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟩
TM-GAC+IX		🟩	🟩	🟩	🟩	🟩	🟥	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
US-CB		🟩	🟩	🟩	🟩	🟩	🟢	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟢	🟩
US-MCM+PAC		🟩	🟩	🟩	🟩	🟩	🟨	🟩	🟩	🟩	🟩	🟦	🟦	🟦	🟦	🟦
PT-GAC+IX	100-200%	🟩	🟢	🟩	🟩	🟩	🟥	🟨	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
PT-IX+CB+NWM		🟥	🟥	🟩	🟨	🟨	🟥	🟥	🟩	🟨	🟧	🟩	🟩	🟩	🟩	🟩
RF-CB		🟩	🟩	🟩	🟩	🟩	🟥	🟥	🟩	🟨	🟥	🟩	🟩	🟩	🟩	🟩
TM-NWM+CB+IX		🟩	🟩	🟩	🟩	🟩	🟥	🟨	🟩	🟩	🟢	🟩	🟩	🟩	🟩	🟩
TM-GAC+IX		🟩	🟩	🟩	🟩	🟩	🟥	🟨	🟩	🟩	🟩	🟨	🟩	🟩	🟨	🟩
US-CB		🟩	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟨	🟩	🟩	🟢	🟩
US-MCM+PAC		🟩	🟩	🟩	🟩	🟩	🟥	🟧	🟩	🟩	🟨	🟦	🟦	🟦	🟦	🟦
PT-GAC+IX	0 - 200%	🟩	🟨	🟩	🟩	🟩	🟥	🟢	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
PT-IX+CB+NWM		🟥	🟥	🟩	🟩	🟢	🟥	🟥	🟩	🟩	🟨	🟩	🟩	🟩	🟩	🟩
RF-CB		🟩	🟩	🟩	🟩	🟩	🟥	🟥	🟩	🟨	🟥	🟩	🟩	🟩	🟩	🟩
TM-NWM+CB+IX		🟩	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟢	🟩
TM-GAC+IX		🟩	🟩	🟩	🟩	🟩	🟥	🟨	🟩	🟩	🟩	🟢	🟩	🟩	🟢	🟩
US-CB		🟩	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟢	🟩	🟩	🟢	🟩
US-MCM+PAC		🟩	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟦	🟦	🟦	🟦	🟦

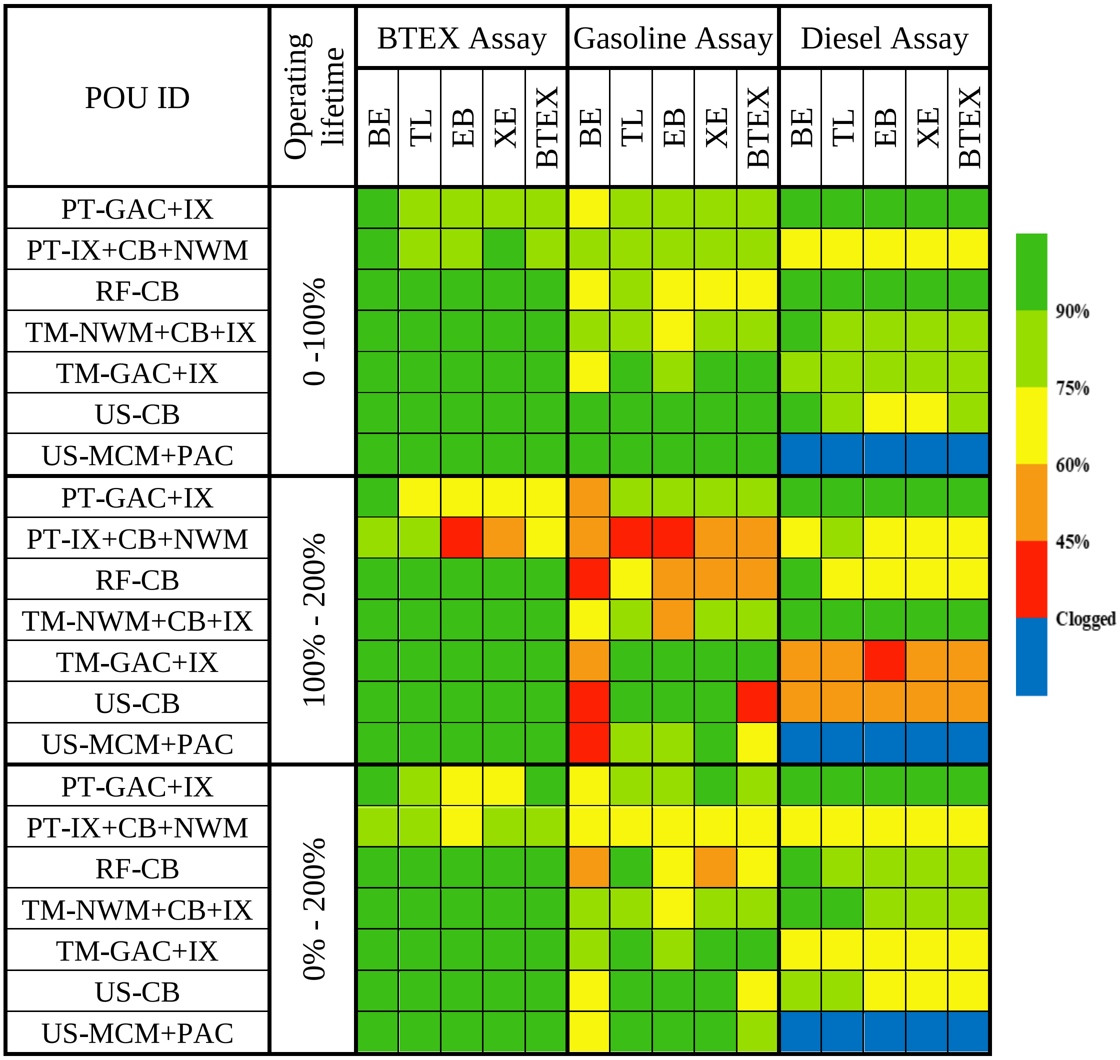
Figure 4.9 Heat map of effluent mean concentrations of the target compounds for three tested hydrocarbons, achieved over 0-100% and 100 - 200% of the operating lifetime of each device

Table 4.2 Ranging value of each compound of BTEX calculated in reference to health-based Canadian standards

Range	0.5 Reg	0.75 Reg	1.25 Reg	1.5 Reg
Benzene (µg/L)	2.5	3.75	6.25	7.50
Toluene (µg/L)	30	45	75	90
Ethylbenzene (µg/L)	70	105	175	210
Xylenes(µg/L)	45	68	112	135

4.4.2 Assessment of point-of-use devices in BTEX removal

As shown in Figure 4.10, the heat map of fractional removal efficiency of the four target compounds in 3 tested fuels, achieved over 0-100% and 100% to 200% of the estimated capacity of each device. The heat map illustrates the percentage of BTEX removal calculated from the difference between effluent and corresponding influent of three assays.



POU ID	Operating lifetime	BTEX Assay					Gasoline Assay					Diesel Assay				
		BE	TL	EB	XE	BTEX	BE	TL	EB	XE	BTEX	BE	TL	EB	XE	BTEX
PT-GAC+IX	0 -100%	🟩	🟢	🟢	🟢	🟢	🟨	🟢	🟢	🟢	🟢	🟩	🟩	🟩	🟩	🟩
PT-IX+CB+NWM		🟩	🟢	🟢	🟩	🟢	🟢	🟢	🟢	🟢	🟢	🟨	🟨	🟨	🟨	🟨
RF-CB		🟩	🟩	🟩	🟩	🟩	🟨	🟢	🟨	🟨	🟨	🟩	🟩	🟩	🟩	🟩
TM-NWM+CB+IX		🟩	🟩	🟩	🟩	🟩	🟢	🟢	🟨	🟢	🟢	🟩	🟢	🟢	🟢	🟢
TM-GAC+IX		🟩	🟩	🟩	🟩	🟩	🟨	🟩	🟢	🟩	🟩	🟢	🟢	🟢	🟢	🟢
US-CB		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟢	🟨	🟨	🟢
US-MCM+PAC		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟦	🟦	🟦	🟦	🟦
PT-GAC+IX	100% - 200%	🟩	🟨	🟨	🟨	🟨	🟧	🟢	🟢	🟢	🟢	🟩	🟩	🟩	🟩	🟩
PT-IX+CB+NWM		🟢	🟢	🟥	🟧	🟨	🟧	🟥	🟥	🟧	🟧	🟨	🟢	🟨	🟨	🟨
RF-CB		🟩	🟩	🟩	🟩	🟩	🟥	🟨	🟧	🟧	🟧	🟩	🟨	🟨	🟨	🟨
TM-NWM+CB+IX		🟩	🟩	🟩	🟩	🟩	🟨	🟢	🟧	🟢	🟢	🟩	🟩	🟩	🟩	🟩
TM-GAC+IX		🟩	🟩	🟩	🟩	🟩	🟧	🟩	🟩	🟩	🟩	🟧	🟧	🟥	🟧	🟧
US-CB		🟩	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟥	🟧	🟧	🟧	🟧	🟧
US-MCM+PAC		🟩	🟩	🟩	🟩	🟩	🟥	🟢	🟢	🟩	🟨	🟦	🟦	🟦	🟦	🟦
PT-GAC+IX	0% - 200%	🟩	🟢	🟨	🟨	🟩	🟨	🟢	🟢	🟩	🟢	🟩	🟩	🟩	🟩	🟩
PT-IX+CB+NWM		🟢	🟢	🟨	🟢	🟢	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
RF-CB		🟩	🟩	🟩	🟩	🟩	🟧	🟩	🟨	🟧	🟨	🟩	🟢	🟢	🟢	🟢
TM-NWM+CB+IX		🟩	🟩	🟩	🟩	🟩	🟢	🟢	🟨	🟢	🟢	🟩	🟩	🟢	🟢	🟢
TM-GAC+IX		🟩	🟩	🟩	🟩	🟩	🟢	🟩	🟢	🟩	🟩	🟨	🟨	🟨	🟨	🟨
US-CB		🟩	🟩	🟩	🟩	🟩	🟨	🟩	🟩	🟩	🟨	🟢	🟢	🟨	🟨	🟨
US-MCM+PAC		🟩	🟩	🟩	🟩	🟩	🟨	🟩	🟩	🟩	🟢	🟦	🟦	🟦	🟦	🟦

Figure 4.10 Heat map of fractional removal efficiency for the target compounds for three tested fuels, achieved over 0-100% and 100% to 200% of the estimated capacity of each device

For the BTEX assays, pour-through filters were the least performant (75% < TL, EB, XE < 90%) during the 100% of the estimated capacity, and their efficiency declined to 60% during 100-200% of the capacity. The removal efficiency of the PT-IX+CB+NWM device was less than the PT-GAC+IX if the usage period was extended. The performance of the PT-IX+CB+NWM device for removal of ethylbenzene and xylenes were less effective (38% for EB and 59% for XE) (Figure 4.10). Nevertheless, their resulting concentrations meet the Canadian guidelines (Figure 4.9). When gasoline is the source of BTEX, smaller removals are observed for benzene, which is more water soluble compared to other BTEX compounds. In Figure 4.11, benzene removal performance of the tested POU units for gasoline assay is plotted from 0 to 200% of the estimated lifetime. The under-the-sink types of POUs showed sustained removal of benzene during their estimated capacity (0-100% of capacity). In contrast, the PT-GAC+IX, TM-NWM+CB+IX and RF-CB filters experienced benzene breakthrough after 50%, 25% and 50% of their capacities. The US-CB POU experienced a progressive breakthrough after 100% capacity. Regardless of the high performance of US-MCM+PAC until 100% of its capacity, the removal efficiency decreased dramatically so that at 200% of the capacity of the filter, desorption of benzene was observed.

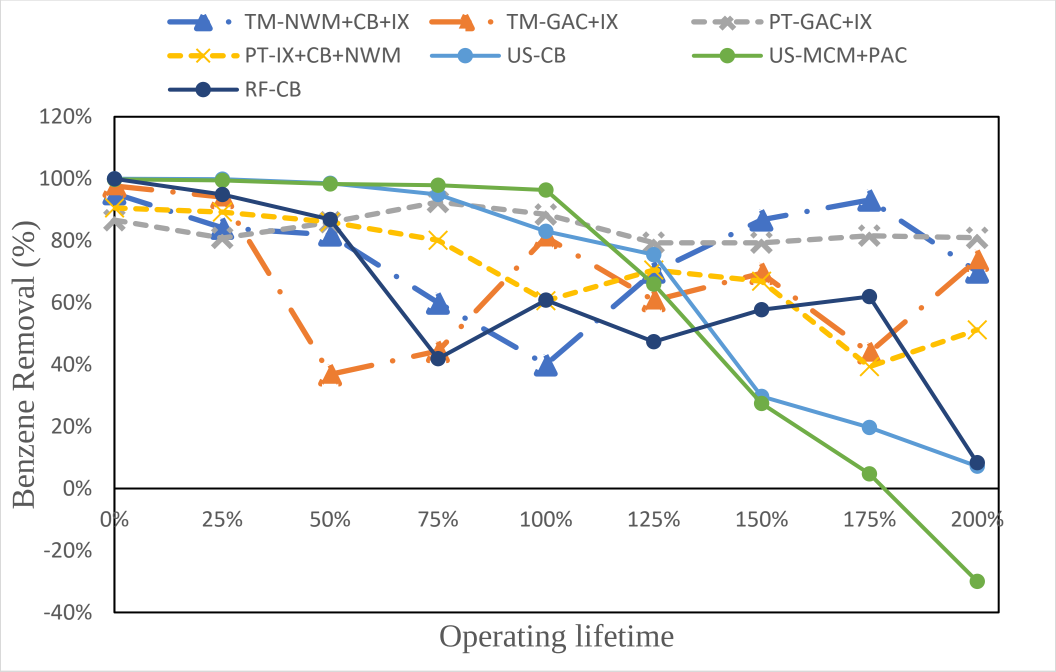


Figure 4.11 Benzene removal performance over 0 to 200% of the capacity of tested POU units for gasoline assays

The time series of toluene removals for the tested point-of-use units for the gasoline assays are summarized in Figure 4.12. As shown, toluene removal is steadier than for benzene, reflecting the smaller losses through volatilization. Tap-mounted and under-the-sink POU units composed of carbon block were adequate for the removal of toluene (> 90%) over the entire range of 0 to 200% of their estimated capacities. The US-MCM+PAC unit had the similar behavior for the removal of toluene and benzene, the breakthrough occurred after operating lifetime, but removal efficiency of toluene decreased slightly over the time, and the performance did not dip below 63%. The PT-IX+CB+NWM and RF-CB unit showed the least toluene removal. A wide range from 24% to 95% for toluene removal is observed in Figure 4.12 for PT-IX+CB+NWM filter, and its breakthrough happened after passing 75% of the capacity.

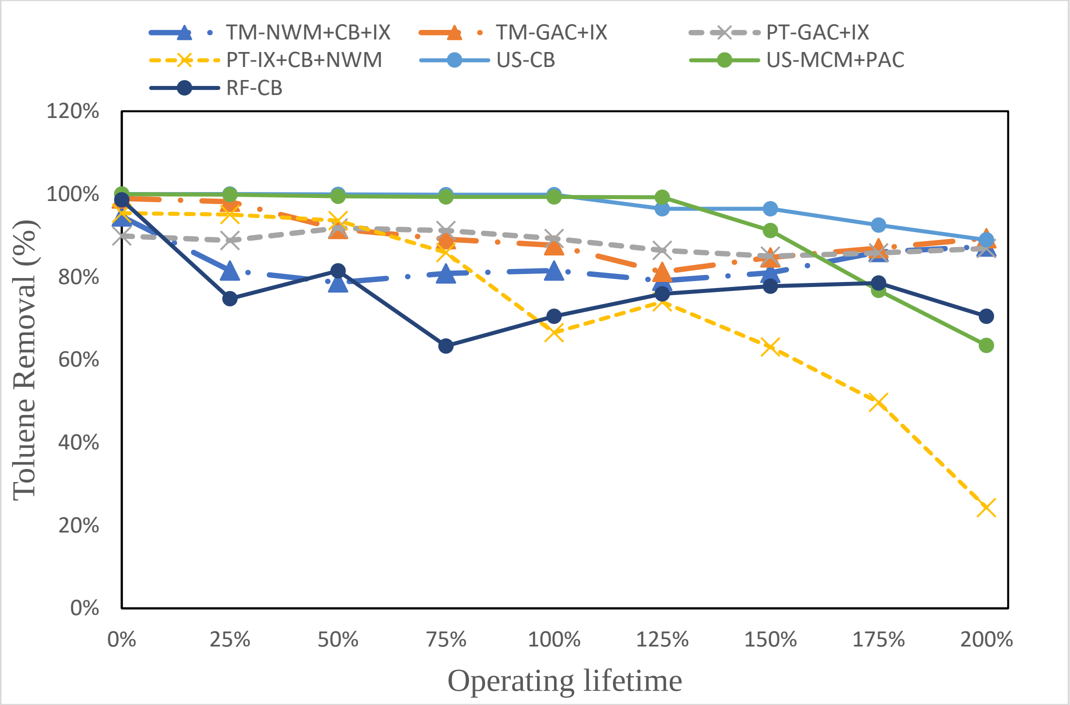


Figure 4.12 Toluene removal efficiency for tested point-of-use unites over 0 to 200% of their capacities for gasoline assays

In Figure 4.13, ethylbenzene removals are shown for the various tested point-of-use units over 0 to 200% of their capacities in gasoline assays. The TM-NWM+CB+IX, PT-IX+CB+NWM and RF-CB filters showed breakthrough right from the initial of their lifetime. Corresponding wide ranges of ethylbenzene removals are observed (from 37 to 94% for RF, 37 to 91% for PT and 37% to 96% for TM). The PT-GAC+IX consistently removed 90% of ethylbenzene from the beginning of its usage until 200% of the capacity.

As the heat map and the removal time series of BTEX compounds showed, the less water-soluble and the higher molecular weight compounds (ethylbenzene and xylenes) were removed more effectively than benzene and toluene (Figure 4.13 and Figure 4.14). Thus, xylenes are the most stable compound among other BTEX in adsorption and desorption. All point-of-use devices have similar behavior on the removal of xylenes compared to ethylbenzene and toluene. PT-

IX+CB+NWM filter again breaks through sooner than the other POUs at 100% of the capacity, and after PT-IX+CB+NWM, RF-CB had the lowest efficiency in removal of xylenes (Figure 4.14).

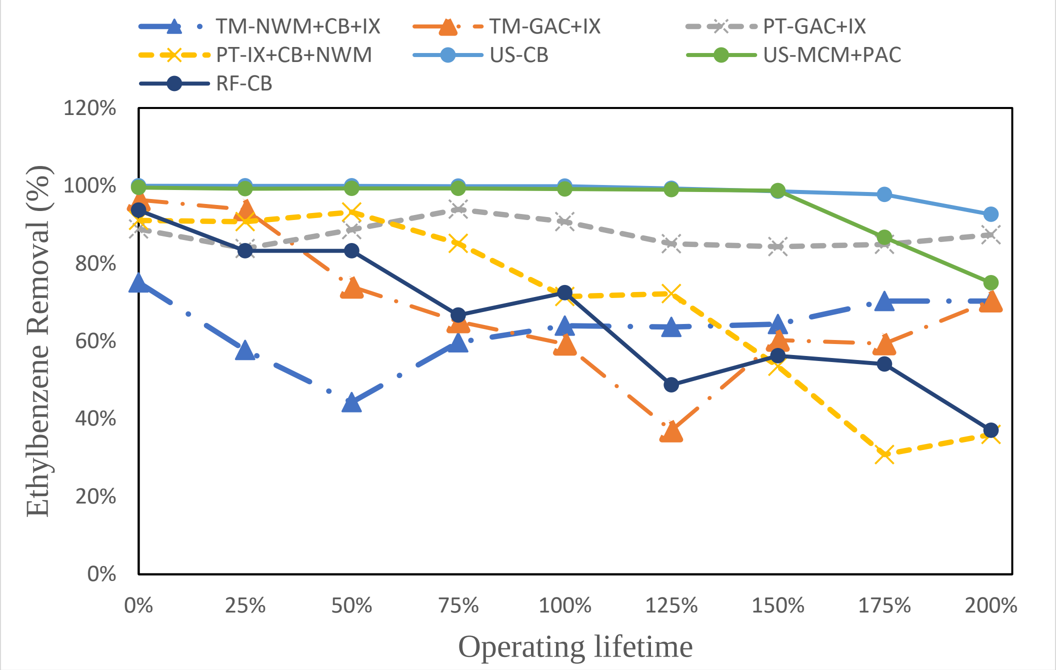


Figure 4.13 Ethylbenzene removal efficiency for tested point-of-use units over 0 to 200% of their capacities for gasoline assays

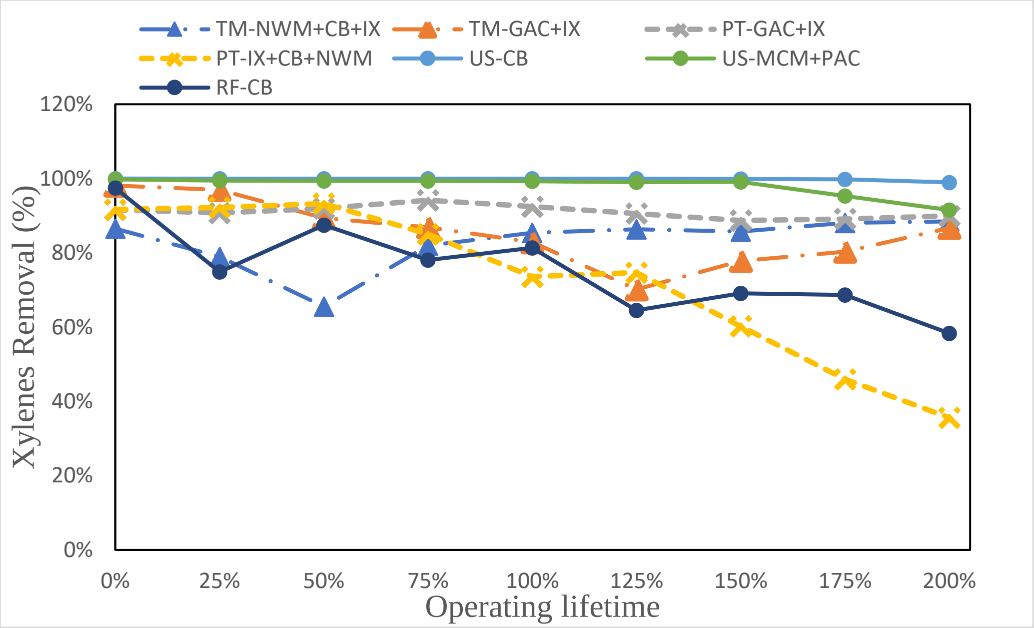


Figure 4.14 Xylenes removal efficiency for tested point-of-use unites over 0 to 200% of their capacities for gasoline assays

Removals by all POU units over 0 to 200% of their operating lifetime are presented in Figure 4.15 to Figure 4.18 when diesel is the source of BTEX. The pour-through filter (PT-IX+CB+NWM) and refrigerator cartridge (RF-CB) presented the best performance of all devices tested for the removal of all BTEX compounds. It should be noted that the influent mean concentration of total BTEX for these two filters were the lowest ones (106±35 µg/L and 123±34 µg/L). Consequently, the high removal fraction values of these filters, are not merely subject to the performance of these filters for the removal of BTEX, it could also reflect the low concentration of influent. Nevertheless, high removals ranging from 77% to 98% are achieved by the two filters (PT-IX+CB+NWM and RF-CB) operated under 200% of their estimated capacities. The removal performance is maintained even beyond their capacity if the filters are operated up to 200% of their lifetime.

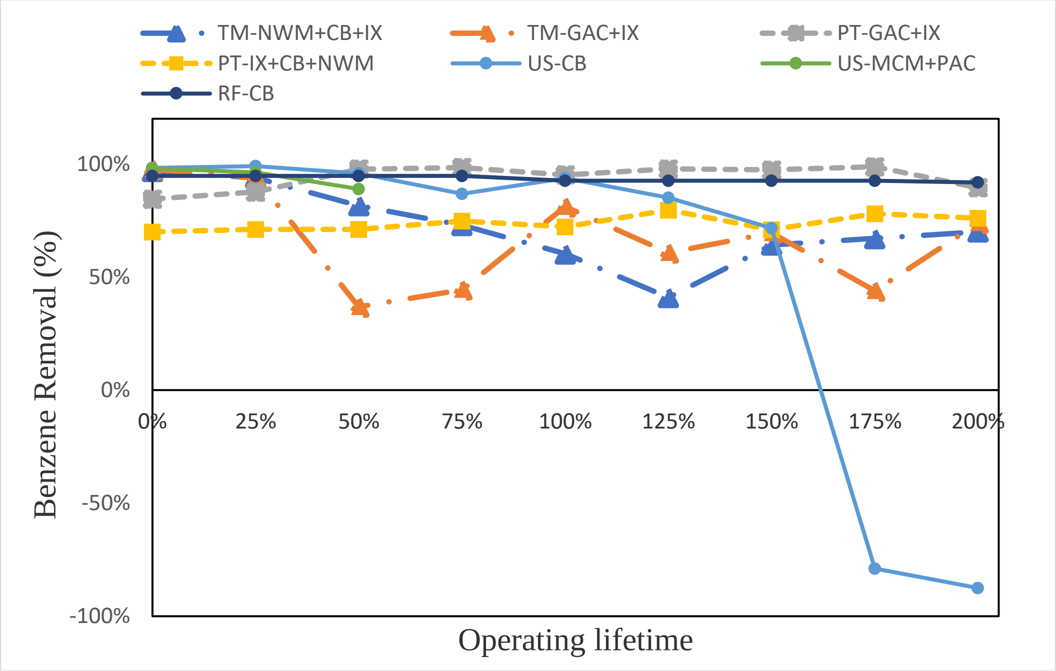


Figure 4.15 Benzene removal performance over 0 to 200% of the capacity of tested POU devices for diesel assay

The US-MCM+PAC stopped operating after 50% of its capacity during the diesel assay which contrasts with the performance of under-the-sink point-of-use filters observed during the gasoline assay, As the removal time series illustrates, the breakthrough started at 25% of the lifetime and the filter clogged at 50% of its capacity. This filter is made of two-stage, and it is possible that the multi-composite media in the first stage clogged prior to the maximum capacity of carbon block in the second stage. The US-CB device removed benzene to concentrations below detection limits up to 125% of the lifetime. Afterward, benzene removal decreased dramatically, and desorption was observed when the POU was operated beyond 150% of its capacity. In contrast, this filter produced highly variable results with other compounds of BTEX. The removals were from 60% to 100% for toluene, 38% to 100% for ethylbenzene and 53% to 100% for xylenes and their breakthrough occurred at 25 % of the estimated capacity.

As the toluene removal time series demonstrated, the performance of the TM-NWM+CB+IX and TM-GAC+IX and PT-IX+CB+NWM units improved within 125 to 200% of estimated capacities. The variation in influent concentrations could only explain such behavior (Figure 4.16).

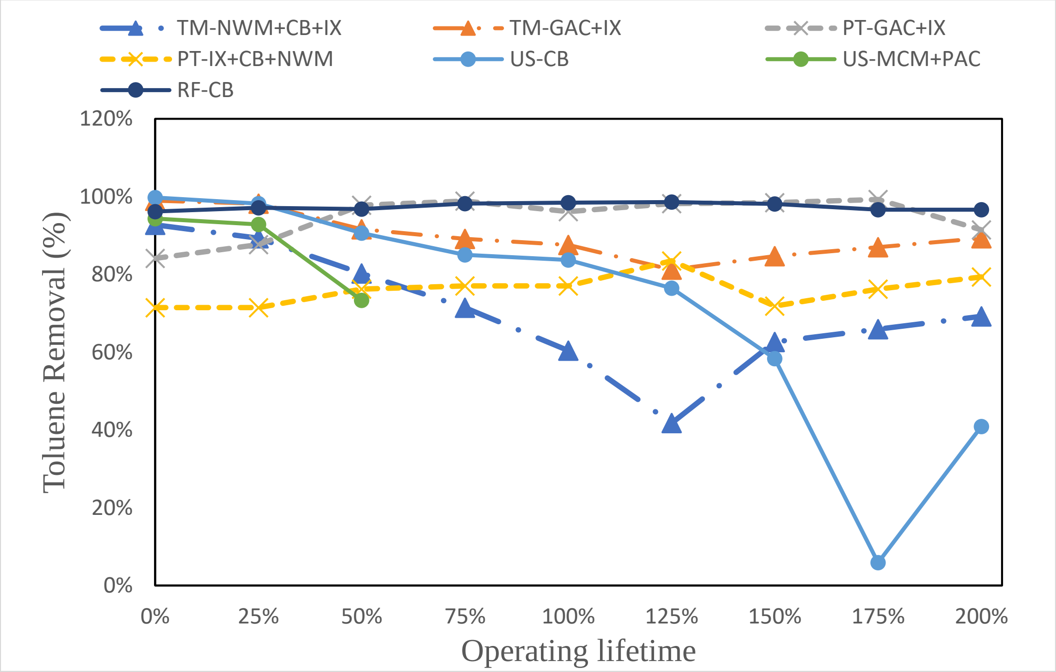


Figure 4.16 Toluene removal performance over 0 to 200% of the capacity of tested POUS for diesel assays

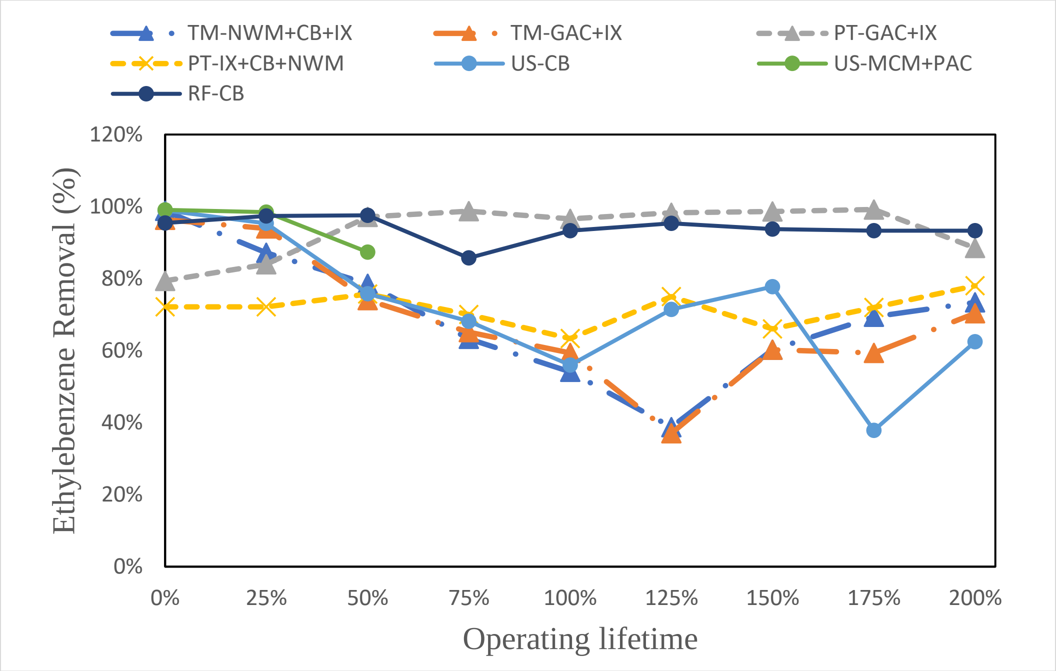


Figure 4.17 Ethylbenzene removal performance over 0 to 200% of the capacity of tested POUS for diesel assays

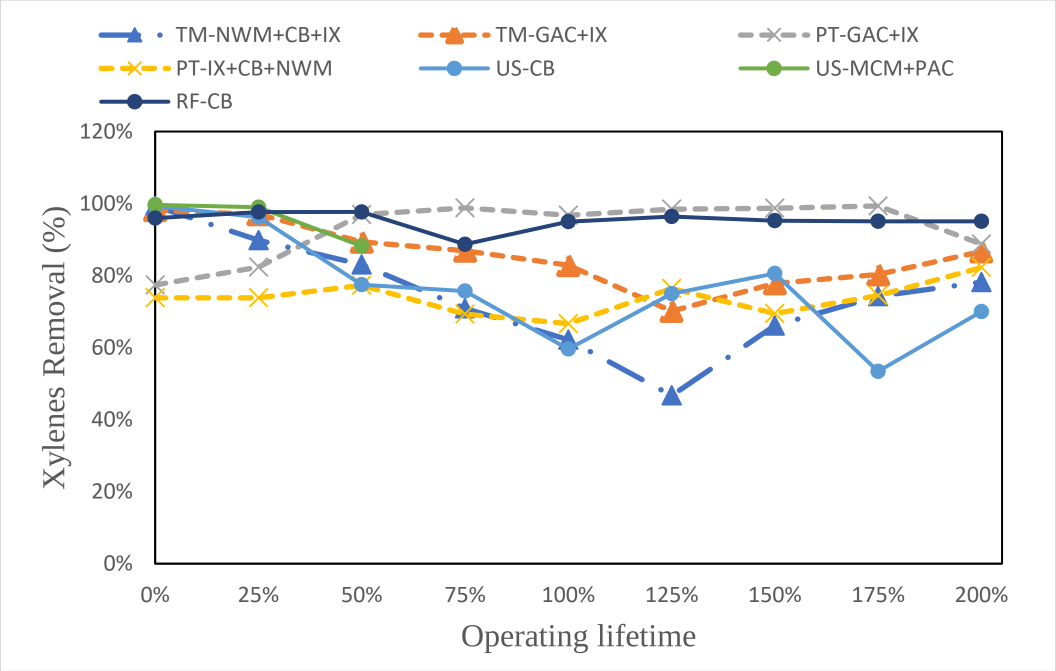


Figure 4.18 Xylenes removal efficiency for tested point-of-use unites over 0 to 200% of their capacities for diesel assays

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1 Main findings

This research project investigated seven point-of-use carbon-based home filters as a temporary alternative for treatment of drinking water contaminated by the spill of petroleum fuel. Our focus was on the removal of benzene, toluene, ethylbenzene and three isomers of xylenes. In this chapter, the findings with regards to the initial research questions are summarized.

The initial questions were:

- Are the POU devices efficient for the removal of hydrocarbon contaminants from drinking water?
- Which types of POU devices are best suited for the removal of HC from drinking water?
- Are the NSF volatile organic compounds (VOCs) reduction claims by POUs verified?
- Do the performance of POU units vary for different mixtures of hydrocarbons (BTEX, gasoline, and diesel)?
- Are the fouled POU devices susceptible to desorb accumulated contaminants to treated water?

The following conclusions are reached concerning the performance of POU units for the removal of BTEX:

1) For a mixture of BTEX diluted in tap water:

- The most performant POU devices were tap-mounted filters and refrigerator cartridge. These devices removed all initial feed and no BTEX were detected in effluents.
- Under-the-sink units presented BTEX removals 100%, as well, but for an influent with lower concentration compared to the TP and RF types.
- The least effective POU in the removal of BTEX were the pour-through units which were not certified by NSF 53 for VOC removal; the average BTEX removals were 71% and 85% for PT-GAC+IX and PT-IX+CB+NWM. Nevertheless, benzene and toluene effluent concentrations of PT-IX+CB+NWM were not below Canadian guidelines.

Figure 5.1 presents an overview of the performance of all POU units for the removal of total BTEX for three assays (a mixture of BTEX, gasoline, and diesel).

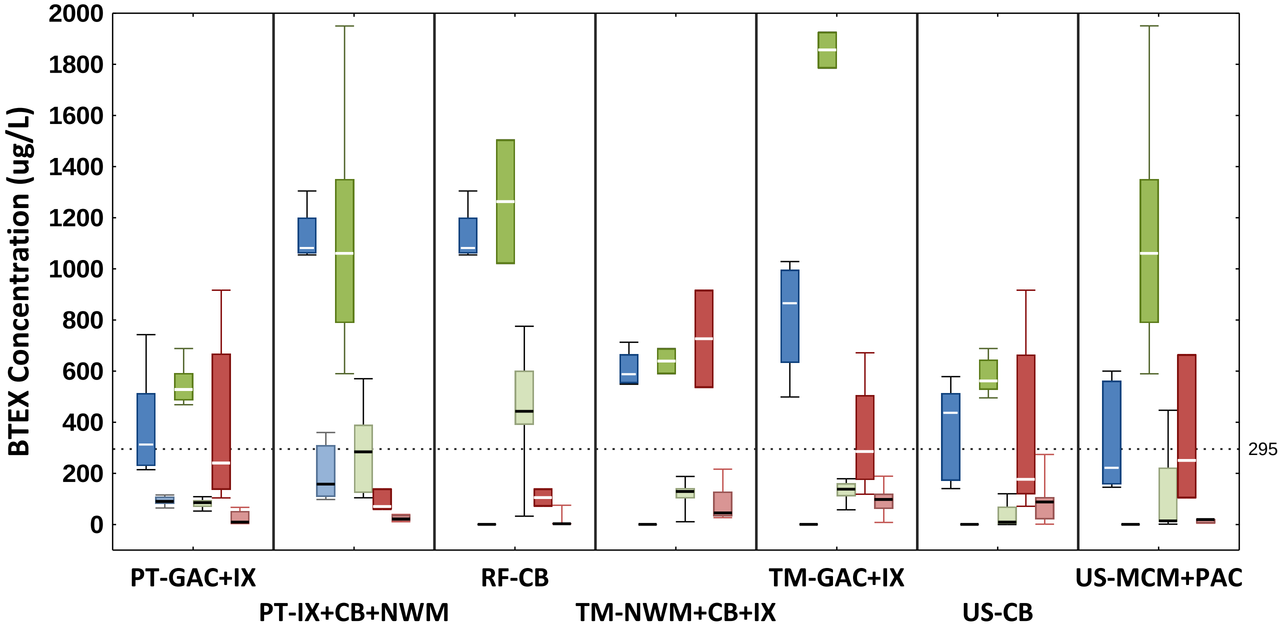


Figure 5.1 Performance of all POU units for removal of total BTEX for three tests (a mix of BTEX, gasoline, and diesel). Boxes represent 25th-75th percentiles, whiskers min-max values, and the square shows median concentrations.

2) **For gasoline diluted in tap water:**

- The most operative POU unit was the carbon-blocked under-the-sink (US-CB) filter for which the lowest concentration of BTEX in the effluent was observed. This device was efficient at removing benzene over the operating life, but not two times of the lifetime.
- The high proportion of benzene and toluene in gasoline is a more significant challenge to the POUs and resulted in corresponding higher concentrations of benzene and toluene in the influents. Our challenge BTEX concentrations were much higher than environmental concentrations reported from environmental monitoring of these compounds in surface water after a spill. Nevertheless, benzene removal performance exceeded 90% for under-the-sink, more than 75% for tap-mounted and more than 60% for pour-through and refrigerator cartridge over their operating lifetime.

- Although ethylbenzene had the lowest ratio among other compounds of BTEX in gasoline, the detected concentrations in effluents exceeded the odor threshold (1.6 µg/L) but remained below the Canadian guideline (140 µg/L).

3) For diesel diluted in tap water:

- The influent BTEX concentration was lower for the diesel assay than for the gasoline and a pure BTEX assays. The diesel assay reflects more the reality of a low background contamination. In that situation, all point-of-use units were efficient for removal of BTEX.
- All POU devices removed benzene effectively over 90% excluding US-CB (> 75%) and PT-IX+CB+NWM (> 60%). Furthermore, all devices reduce all BTEX compounds successfully below Canadian health regulation (excluding TM-NWM+CB+IX for xylene).
- Physicochemical characteristics of other compounds present in diesel could be a factor to explain the clogging of one of the under-the-sink POU unit (US-MCM+PAC) after 50% of its operating lifetime.

Key concerns in using these devices in households include: 1) the insufficient removal during periods of water contamination; and 2) the desorption of captured BTEX after concentrations in the influent decrease. Our results suggest that benzene was susceptible to desorption when the initial concentration was high. When gasoline was used as the source of BTEX, some benzene desorption was observed after 125% of the operating lifetime of the filters having the highest operating lifetime (US-CB = 3 800L, US-MCM+PAC = 5 400L and RF-CB = 1 560L).

Overall, this project has shown that point-of-use devices which are certified for removal of BTEX by NSF 53, can be a feasible, immediate and effective solution for drinking water contamination in an emergency caused by an oil spill. However, the selection of the device should be made carefully to ensure the removal of the most toxic compounds. Furthermore, the replacement of the devices after the end of the contamination should be managed diligently.

5.2 Future work

During this project, new questions came up as well as ideas for future research. It would be an interesting research topic to:

- Test the impact of adsorption/desorption of fuel to the pilot while it can be one of the reasons for influent fluctuations.
- Investigate the impact of pH on the efficiency of point-of-use filters.
- Reduce the impact of heterogeneity of initial feed in order to simulate the real scenarios while the micelles of hydrocarbons incline to adsorb.
- Simulate an oil spill to the distributed system of drinking water and estimated the adsorption/desorption and the real BTEX concentration reach to the consumers in tap water.

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