Analysis of Biphenyl and Bis(2-ethylhexyl) phthalate releases and exposure in diverse water bodies in Canada

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Course: Emerging contaminants in the environment: Challenges and Fate

Course number: CIVL 6112

Abstract

In Canada, the environmental impact of biphenyl and bis(2-ethylhexyl) phthalate (also known as DEHP) is a matter of growing concern. While regulatory measures exist to control their release, the persistence of these chemicals poses challenges for Canadian ecosystems. The transport of pollutants across air and water masses knows no borders, making it essential for Canada to engage in international collaborations and adhere to global initiatives aimed at mitigating the transboundary movement of these substances. For this reason, a detailed analysis of biphenyl and DEHP is done to clarify different alterations of these compounds through time and determine how much of them are released based on various facilities across Canada. A comprehensive examination of time-series release data and geographical mapping revealed predominant downward trends in pollution across various Canadian provinces, both in terms of quantity and percentage. Regional scrutiny identified specific areas within each province responsible for most pollutant releases. Furthermore, an assessment of the distribution of compounds across environmental compartments highlighted that air media was the primary receptor of contaminants, surpassing water bodies and land sites. This added some challenges to the project as the objective of this project was to analyze the effects of the contaminants on water bodies, specifically surface water, and groundwater.

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1. Introduction

As Canada's manufacturing and industrial sector continues to grow annually, contaminants of environmental concern have become an issue that has gained traction amongst scientists, environmentalists, regulatory bodies, and the general public (Statistics Canada, 2023). Particularly, the presence of these contaminants in diverse water bodies, and how they transport between different environmental components, such as air and land, needs to be studied to understand the threats to human health and the environment. Canada has implemented a monitoring system, known as the National Pollutant Release Inventory (NPRI) to track the release of over 320 pollutants from over 7000 industrial facilities across Canada (Government of Canada, 2021). The targeted facilities to be monitored are chosen based on 1 of the 3 criteria;

(1) the total hours worked by the employees per year is more than 20,000,

(2) the activities that occur at the facility include incineration, wastewater treatment, fuel combustion or wood preservation,

(3) if the substance is above the reporting threshold for manufacturing, processing, using, or releasing (Government of Canada, 2021).

With cooperating with facilities, the Government of Canada can develop mitigation and prevention strategies to reduce its adverse impact of persistent contaminants, such as biphenyl and bis(2-ethylhexyl) phthalate. Under the Canadian Environmental Protection Act, 1999 (CEPA 1999), the Canadian government regulates various substances to protect the environment and human health. The regulation of the contaminants biphenyl, specifically polybrominated biphenyls (PBB), and polychlorinated biphenyls (PCBs), and bis(2-ethylhexyl) phthalate, also known as di(2-ethylhexyl) phthalate or DEHP, falls under the purview of CEPA, 1999 (CEPA, 1999).

Biphenyl is a naturally occurring compound in nature, as well as anthropogenic. It exists naturally as a component of crude oil and coal tar and can be industrially produced through chemical processes for applications such as electrical equipment, heat exchangers, and hydraulic systems (Government of Canada, 2017; Li, et al., 2016). They also could be used for adhesives and plastics if they were mixed with chemicals such as plasticizers and fire retardants (Erickson et al., 2011). Biphenyl can enter the environment through multiple pathways; air, water, sediments, and land (Beyer, et al., 2009). Whether that is through accidental spills, improper disposal, volatilization from soil to water, incineration of waste to name a few (Beyer, et al., 2009). While biphenyl is generally considered to have low toxicity, its derivatives like polychlorinated biphenyls are endocrine disrupting chemicals (EDC), meaning it can affect the hormones and reproductive cycle of organisms (Buha Djordjevic, et al., 2020). Additionally, biphenyl is a persistent organic pollutant (POPs), meaning they have the capability for long-range atmospheric transport (LRAT), they are resistant to environmental degradation, and they can bioaccumulate in the food chain from aquatic organisms to humans (Johnson, et al., 1964; Li, et al., 2010). It can have a long-term presence in the environment and its systems, which makes it harmful to human health and the environment. Due to these adverse effects, biphenyls and some of their derivatives have been banned around the world, including Canada (Government of Canada, 2017). In 1977, the "import, manufacture, and sale (for re-use) of PCBs" became illegal, in 1985, PCBs release into the

environment became illegal, and in 1989, PBBs were banned in Canada (Government of Canada, 2013; Government of Canada, 2017). However, currently biphenyl derivatives are still being released or found in the environment due to the long-range transport via global air currents, found in hazardous waste sites, and the usage of equipment that contains PCBs, as legislation allows facilities to use PCB equipment until the end of their service life (Government of Canada, 2006; Government of Canada, 2017; Johnson, et al., 1964).

Bis(2-ethylhexyl) phthalate is a synthetic chemical widely employed as one of the most prevalent phthalate plasticizers in use in Canada. Its purpose is to make plastic more flexible, thus it can be found in many products such as cosmetics, food packaging, lubricants, medical devices, paint removers, furniture materials, and personal care products (Meek, et al., 1994; Rowdhwal, et al., 2018; Zarean, et al., 2016). For example, 40% DEHP can be found in soft PVC products like flooring, clothing, and toys (Koch, et al, 2006). These products are either imported or manufactured in Canada. The downside is using DEHP is that since it is not chemically bound to the polymer in the product, it can be easily exposed to humans and the environment. DEHP can be removed from the product through repeated use, heating, weathering and/or cleaning of the product. From this, its exposure pathway to the environment and humans includes leaching, and migration within the atmosphere (Koch, et al, 2006). It can also be released in the environment through industrial and manufacturing uses and discharges, and waste disposal sites (Government of Canada, 1994; Rowdhwal, et al., 2018). Due to all these exposure pathways, DEHP can be generally found in the soil, water, and air (Rowdhwal, et al., 2018). In terms of how humans and organisms are exposed to DEHP, it can be through the process of ingestion of contaminated food and water, inhalation of dust particles that are attached to DEHP, and continuous physical contact (Koch, et al, 2006, Rowdhwal, et al., 2018). According to *Persistence and Bioaccumulation Regulations* in CEPA, 1999, DEHP is not persistent nor does it bioaccumulate in the environment or humans as phthalates can biodegrade (Canada, 2000). However, the degradation process in sediment and soil is slower when oxygen conditions are low. Even though DEHP does not have a long-term lifespan in the environment, it has raised concerns with respect to the adverse effects on human health and the environment. The primary health impacts are on the endocrine system, neurodevelopment, and respiratory systems, as well as hepatoxic and cardiotoxic effects on organisms (Koch, et al, 2006; Rowdhwal, et al., 2018; Zarean, et al., 2016). Some of these health effects can be long-term depending on the exposure. Under CEPA, 1999, DEHP is considered toxic. Currently, DEHP has been banned in cosmetics since 1944, and it is regulated in children's articles and toys that contain vinyl (Canada, 2010; Government of Canada, 2020). Under the *Food and Drugs Act*, DEHP in medical devices and food are not banned nor regulated, but they are monitored by the *Medial Devices Regulations*, Canadian Total Diet Study and Canadian Food Inspection Agency (CFIA) (Government of Canada, 2020).

Both contaminants have pathways where they navigate the environment in a diverse manner, with air, water, and land serving as conduits for their dispersion. Additionally, with having a wide range of adverse effects, it is important to fully understand how it interacts with environmental components within Canada. It is vital to understand how these contaminants are being released into the environment from an industrial point of view to be able to mitigate and limit its

implications. As there are limited quantifiable data and studies, this study aims to provide a clearer perspective on the documented point sources of biphenyl and bis(2-ethylhexyl) phthalate.

1.1. Objective

The aim of this study to compare the release of the following pollutants, biphenyl and bis(2-ethylhexyl) phthalate, from different facilities across Canada and projecting their presence in diverse water bodies (surface and groundwater) as best as possible given the NPRI database.

The research objective includes:

1. Comparing the release of pollutants across Canada between provinces, environmental compartments, facility types for 10 years.

2. Assess the release of plastic pollution from bis(2-ethylhexyl) phthalate in facilities given the total waste released by the facilities.

3. Model the burden of these chemicals in the environment in the coming years based on facility prevention/treatment activities.

Upon achieving these objectives, a more comprehensive understanding of biphenyl and bis(2-ethylhexyl) phthalate in the Canadian context can be furnished. The aim is to observe how Canadian water bodies have been affected by these substances, through an array of different industries such as the synthetic fiber industry and the pulp and paper industry. With this data, the goal is to be able to forecast the future trend of these CECs, so effective preventative, assessment, and management procedures are in place to ensure Canada is protecting the health of the environment and organisms.

1.2. Study Area

All of Canada's provinces and territories are considered in the study area for the contaminants of interest. However, the information and data provided were only from Ontario, British Columbia, Alberta, Quebec, Nova Scotia, Saskatchewan, Manitoba, and Newfoundland and Labrador due to data constraints. The 2 contaminants were analyzed through the environmental components of water, air, and land.

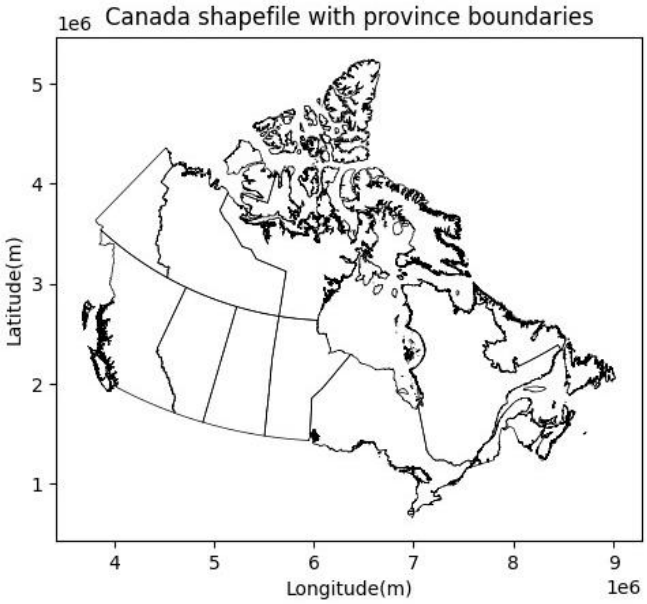

Figure 1-Map of Canada

2. Methodology

2.1. Overall Data Collection

In this study, NPRI database was used as the input of the models from Environment Canada. This dataset encompasses the releases of various pollutants across Canada from different facilities.

Within this huge dataset, there are 910,182 emission observations and 18 features, like the year of ejection, pollutant's name, code, amount, province, etc. Also, about 275 unique compounds are reported from 1993 until 2021, among which biphenyl and bis(2-ethylhexyl) phthalate records show 666 and 623 yearly releases to different media of the environment. There are 4 categories of target mediums into which the pollutants are released, air, land, water bodies, and any of these media but with amount of less than one tonne.

2.2. MATLAB Algorithm for Time-Series Data Analysis and Prediction

As the input for the models is provided, a MATLAB-based algorithm is primarily developed for data preprocessing and analysis. Within this algorithm all the missing data are detected and indicated as time lags in time-series diagrams. For the provinces where there is no relevant or efficient information, diagrams are reported with a "no data available" text to manifest the lack of data in some territories or years. Besides, "polyval" and "polyfit" functions are used to determine the trendline characteristics to predict the burden of the compounds in the coming years. Also, coefficient of determination is utilized for indicating the accuracy of the first-degree polynomial fitted lines to the last 10 years of data.

2.3. Python Algorithm for Data Mapping

This algorithm uses different type of input, which is Canada's shapefile. This shapefile is downloaded from "Statistics Canada" and then enters the mapping process. Afterwards, each of the provinces are separated from the whole Canadian shapefile using column-name selection and geo-pandas library. Each of the province shapefiles are projected from a metric geolocational data to decimal-degree longitude and latitudes by the implementation of "to_crs()" function. After that, for each specific year, the company or facility's name is read in the NPRI-release-reject .csv file, which contains all the release information, and the same company or facility is searched in the NPRI-geolocational .csv file, which includes the longitude and latitude of companies and facilities. Those geolocational data are plotted using "matplotlib" library. Eventually, to check if the process is working accurately, a point-checker or "Point(lat, lon)" as well as "contains()" functions are added to the final steps of the procedure via "shape-geometry" library which export logical values of whether the company or facility's location exists in the provincial boundary.

2.4. Spatial Analysis of Facility-Based Release Incidents via Excel

The release inventory sheet did not include the location of the release incident. To analyze the spatial distribution of biphenyl and DEHP, the location of each release was assumed to be at the geographic coordinates of the releasing facility. The geographic location (in latitude and longitude) of each facility was acquired from the NPRI's Geolocations sheet. An outer join was performed to assign the latitudes and longitudes to each release by matching the facility name between both sheets. This step was repeated once for biphenyls and once for DEHP. Following the joining step, facilities which did not match a corresponding facility in the geolocation inventory were dropped from the dataset. Fortunately, all facilities had corresponding entries in the geolocation sheet and thus all data was retained. The newly merged, geolocated release dataset was exported as a CSV file and then loaded into QGIS as point objects for further analysis of the spatial distribution.

2.5. Temporal Facility-based Analysis via Excel

To analyze temporal trends in pollutant release by the various industries, each dataset for both contaminants was grouped by the industry (NAICS Title field). Some industries were aggregated due to their similarity (e.g., petroleum refining industries) and to allow for a more manageable comparison across industries. For each industry (or group of industries), the total quantity of release to air, land and water was tallied for each year and recorded. Exploratory plots were generated for the time evolution of release by industry.

Overall, Figure 2 represents the whole modeling processes developed for the NPRI data analysis.

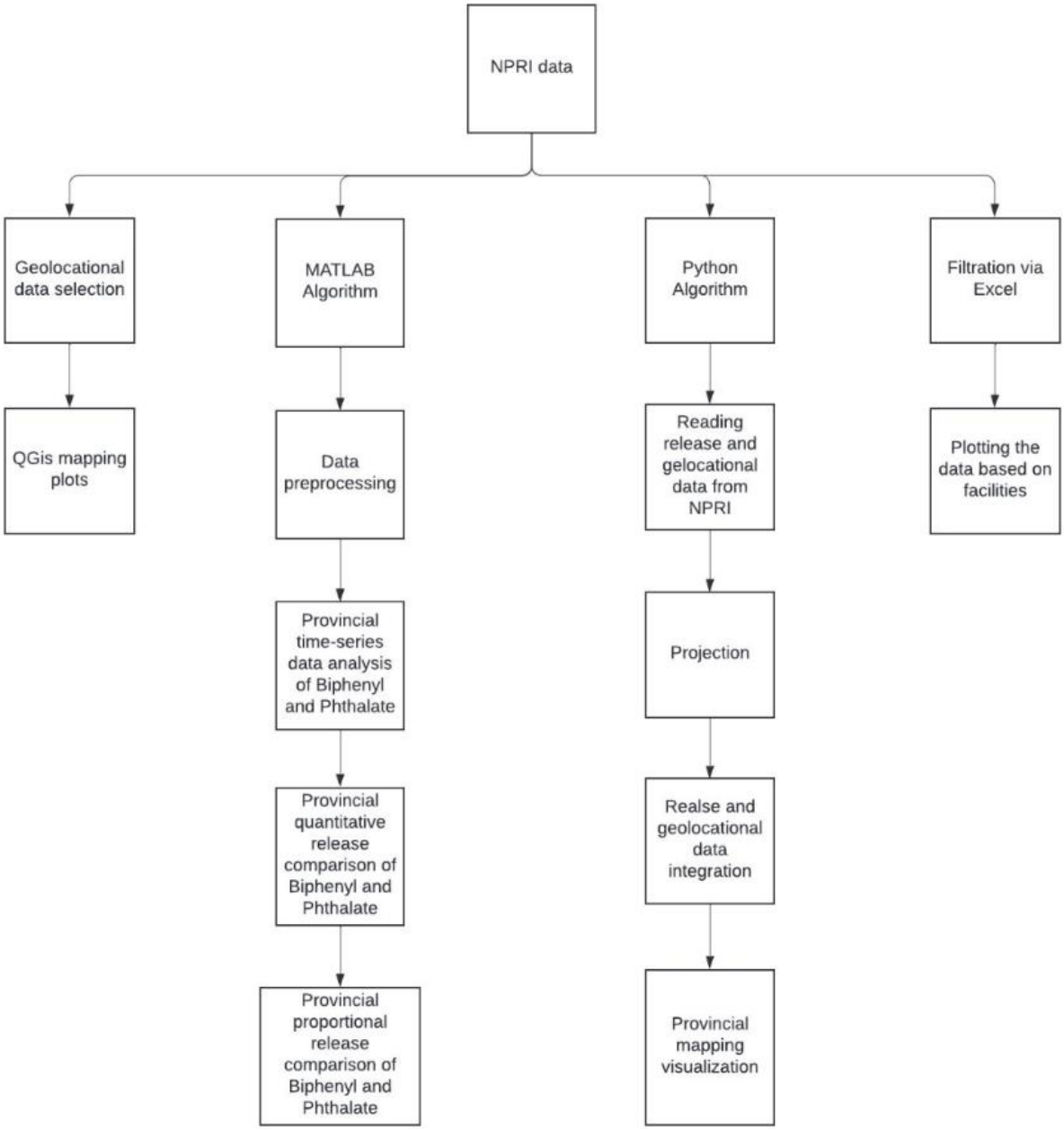

Figure 2-Models developed for the analysis

3. Results and Discussion

3.1. Comparison of Bis(2-Ethylhexyl) Phthalate and Biphenyl Releases Between the Provinces

NPRI release-reject dataset was used for comparing the number of releases of DEHP and biphenyl to the environment. For this reason, a MATLAB-based algorithm was developed which selects each of the provinces available in the NPRI dataset and plots the time-series of desired compounds released from 1993 until 2021 (Figures 3, 4).

For biphenyl, as depicted in Figure 3, there are roughly 7 provinces indicating sufficient data with Ontario (ON) and Manitoba (MB) having around 18 tonnes (the highest) and 13×10^{-4} tonnes (the lowest) overall amount of pollution in the environment respectively. Most of the provinces like Alberta (AB), British Columbia (BC), Ontario, Quebec (QC), and Saskatchewan (SK) are manifesting a decreasing trend (4 to 0.1, 0.06 to 0.005, 18 to 4, 1.5 to 0.1, 1.2 to ≈ 0 tonnes, respectively) in the recent years although there are several fluctuations in BC and AB releases. When it comes to Manitoba, an upward behavior is interpretable, however, the quantities are negligible compared to the other territories ($3 \times 10^{-4} - 15 \times 10^{-4}$ tonnes). Eventually, there has been a growing pattern of biphenyl released to the environment in the provinces such as BC, ON, and QC in the past 3 years.

Bis(2-ethylhexyl) phthalate provincial times-series plot (Figure 4) indicates noticeable downward tendency in Ontario and Quebec provinces (11 to almost 0, 20 to almost zero, respectively), specifically in the recent years of analysis. Furthermore, there are partial data points for Alberta before the year 2000 which depict the same behavior as ON and QC (decreasing from around 17 to 1 tonnes). Finally, for the other provinces, there was no comprehensible information from the NPRI database indicating any releases of our desired compound in the environment.

Based on the quantitative analysis, which is available in the Figure 28 and Figure 29 in the Appendix, Ontario has almost the maximum amount of biphenyl releases starting with around 18 tonnes in 1993, then following an approximately descending trend reaching about 4 tonnes in 2021. In this analysis, Newfoundland and Labrador peaked at nearly 18 tonnes in 2005 with merely one data available in the dataset. In addition, Alberta's information could be seen from the graphs, showing constant negligible values compared to Ontario. Percentage-oriented comparison for biphenyl (Figure 30) demonstrates the predominant role of Ontario in the emission process, nearly reaching 100 percent of releases to the environment. Besides, some other provinces like Alberta and Quebec take part within certain years, which is negligible measured against Ontario.

According to Figure 31, Quebec is almost taking control of total DEHP releases to all natural media although there are some other contributions of phthalate ejection from Alberta and Ontario until 2001, peaking at approximately 10 tonnes. Afterwards, some high fluctuations of phthalate releases in Quebec are observable until 2010, then converging to about zero. Ontario releases are visible almost every year, but with approximately near-zero quantities. Moreover, in the proportional analysis of the DEHP, Ontario and Quebec are engaged in a competitive scenario, yet Quebec constantly surpassing the overall percentage of ejection across most of the years shown in Figure 30 in the Appendix.

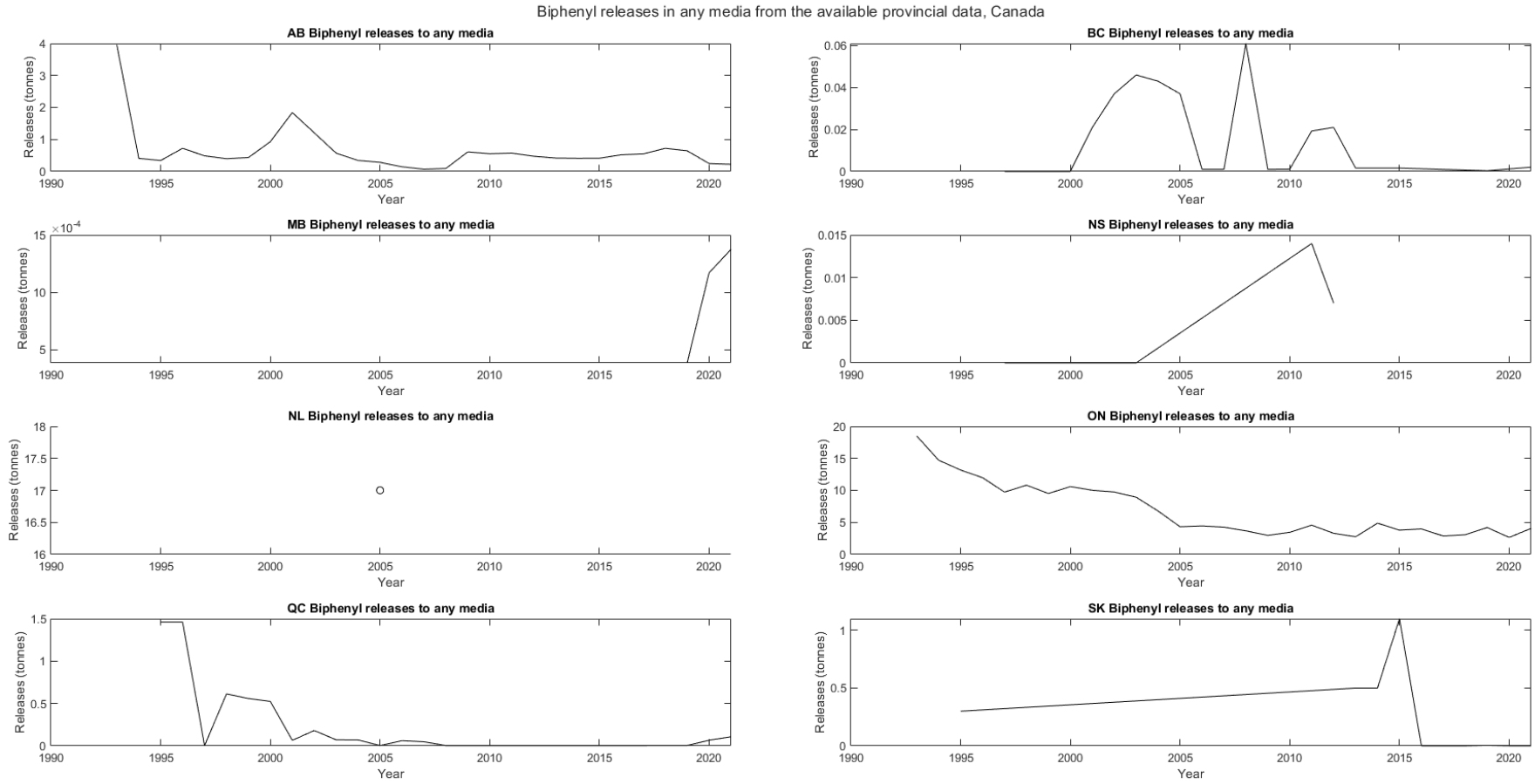

Figure 3-Biphenyl releases compared between the provinces, getting ejected to any media (means the sum of air, land, water, and all media (<1 tonne)).

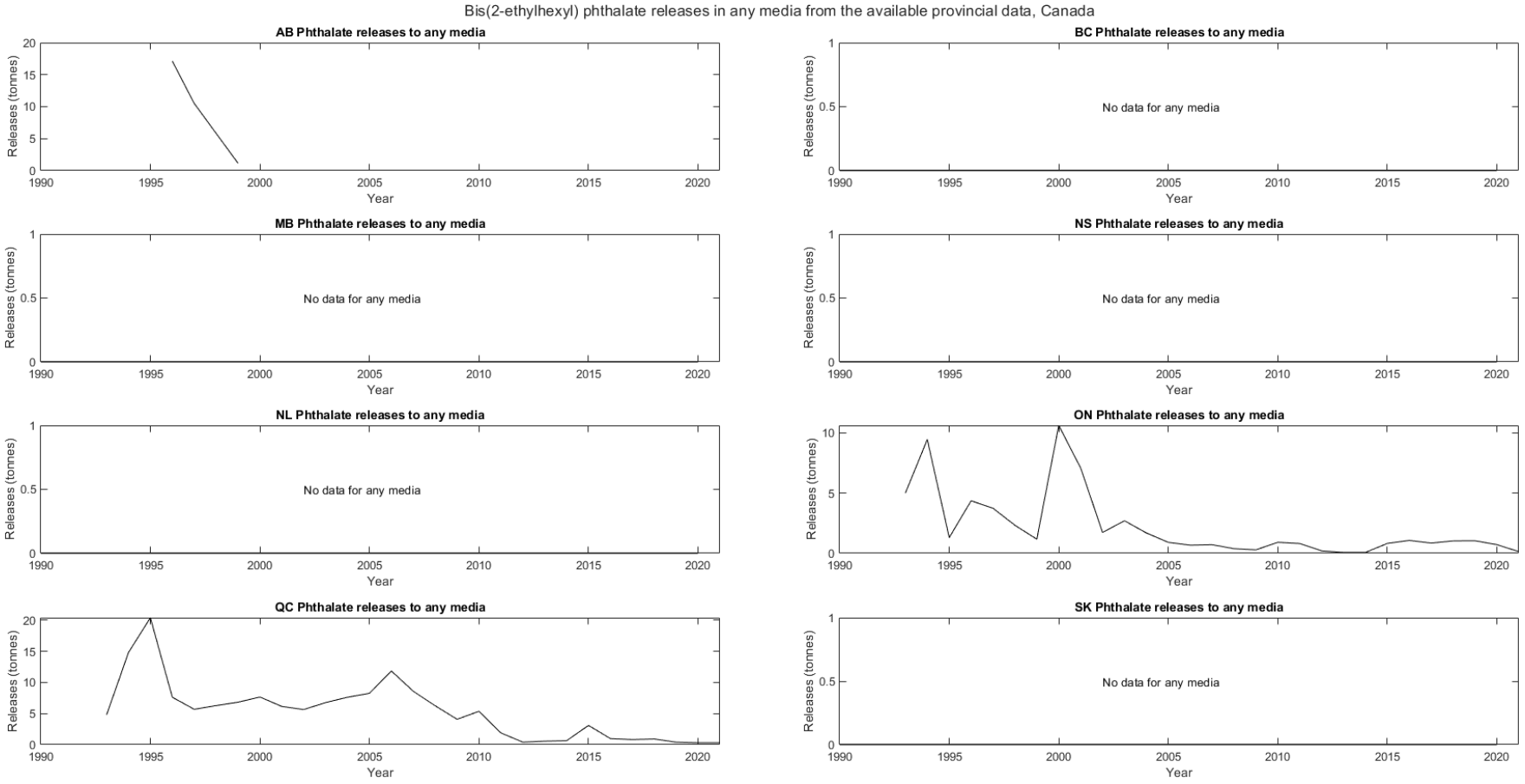

Figure 4-Bis(2-ethylhexyl) phthalate releases compared between the provinces, getting ejected to any media (means the sum of air, land, water, and all media

3.2. *Analysis of Biphenyl and Bis(2-Ethylhexyl) Phthalate Between the Regions*

For the purpose of the regional analysis of biphenyl and DEHP releases across Canada, a Python algorithm was developed which utilizes Canada's shapefile, separates the provinces, projects the geolocations from the metric longitude and latitude data to decimal degree ones, reads the company or facility which has ejected the compound to the environment from NPRI-release-reject dataset and finds the exact geolocations of the company or facility in the exact year in the NPRI-Geolocational dataset. Thus, for each of the years from 1993 until 2021, the results are exported in PNG format as shown in Figure 5 for biphenyl and DEHP.

Biphenyl results in Figure 7 indicate that in Ontario, southern sections of this province like in the vicinity of Windsor, Toronto, Niagara Falls, Peterborough, Ottawa, and minor central parts such as Timmins are producing this contaminant. In British Columbia, Vancouver Island and Central Interior regional districts are ejecting more than the other sections. Moreover, Alberta is contributing to the pollution from the South, Calgary, West Central, North-East and some points of North-East regions. Southern divisions of Quebec like Montérégie and Laurentides, central parts of Nova Scotia province such as the middle of coastal area of Annapolis and Bay of Fundy, and eastern sections of the Cape Breton Island, Prairie North division of Alberta, and South Eastman plus Central sections of Manitoba are the other noticeable locations of releasing the biphenyl in the environment.

Bis(2-ethylhexyl) phthalate maps in Figure 5 demonstrate similar outputs to the biphenyl maps, however, this compound is majorly being ejected to the environment only from Ontario and Quebec given the NPRI dataset. In addition, the locations in Ontario are more concentrated in the south and there are no data points in the central divisions. In Quebec, in addition to Montérégie and Laurentides, there are Estrie and Centre-du-Québec divisions taking part in releasing the DEHP.

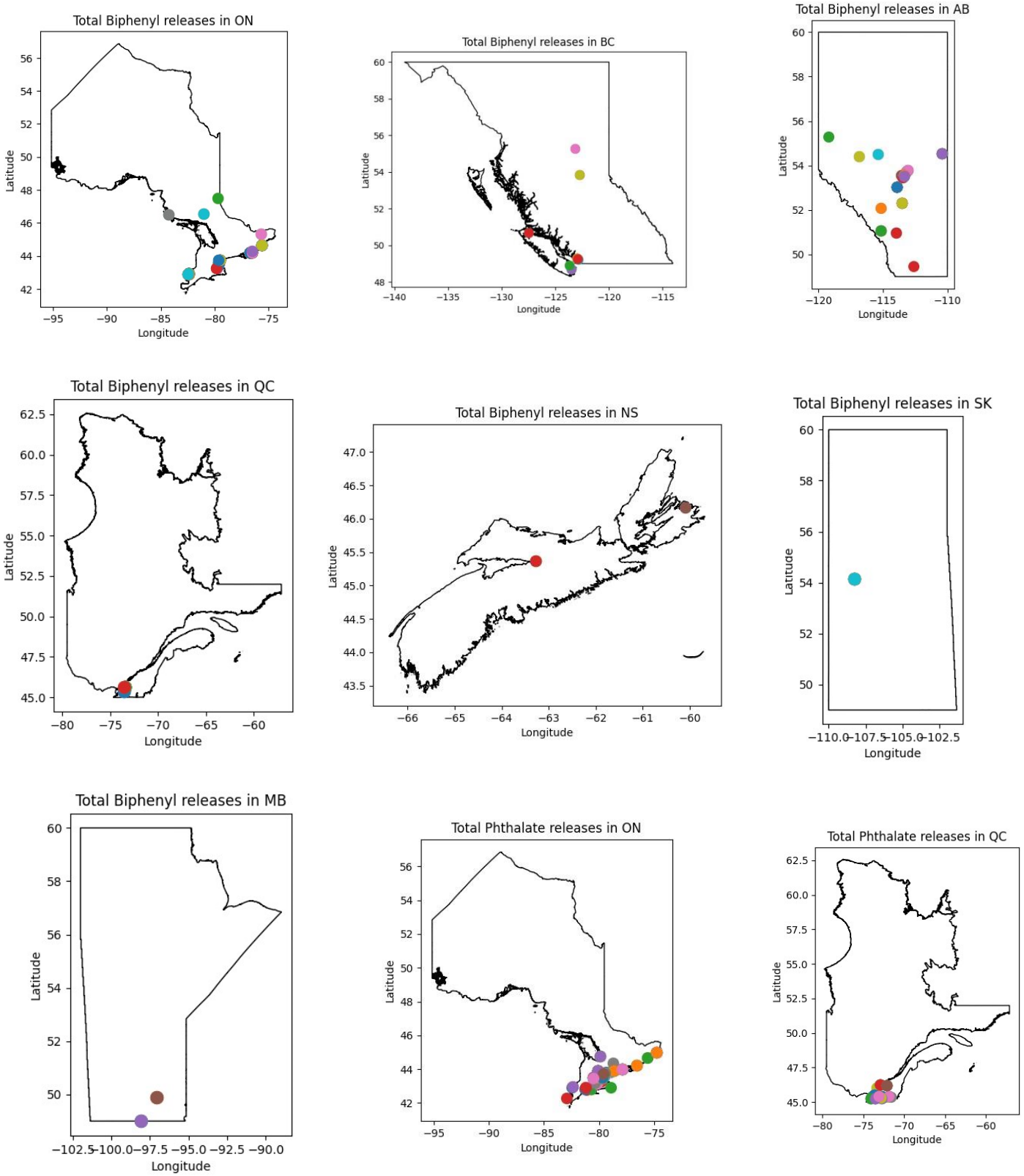

Figure 5-Regional analysis outputs

3.3. Analysis of Biphenyl and Bis(2-Ethylhexyl) Phthalate Between Different Environmental Compartments

There are 4 categories of releases to the environment into which the pollutants are ejected, air, land, water bodies, and any media but with quantities less than 1 tonne. Results indicate that air media is the most burdened environmental compartment among all the categories. Subsequently, almost the same trends are interpretable from the air-related trends shown in Figure 7 as the total releases of biphenyl and DEHP in Figure 3 and Figure 4. For land, the data demonstrates a lack of information from the NPRI dataset both for biphenyl and DEHP since there are no adequate time-series datapoints in Figure 32 and Figure 35.

Based on water compartments, Ontario is the only province containing water-bodies data, in which biphenyl releases have been decreasing throughout the last 20 years and DEHP has only a few datapoints indicating negligible quantities before 2010 as depicted in Figure 33 and Figure 36.

For the fourth category, which is the releases to any compartment but with a value of less than 1 tonne, BC, MB, ON, and QC faced positive trends in the past 5-10 years of biphenyl data, indicating higher quantities of releases in the coming years while AB and SK are behaving inversely (Figure 34). Also, DEHP results show intensive fluctuations of the releases in Ontario and Quebec based on the fourth category yet having a downward tendency in the recent years of available data (Figure 37).

To recap, from the analyzed data, it can be observed that biphenyl and bis(2-ethylhexyl) phthalate, is mostly released into the environment through the air, even though these contaminants can be found in air, water, and land.

These contaminants can enter the environment by

- **Surface water:** Rainfall can wash these contaminants from roads, and industrial sites into nearby surface water bodies.
- **Groundwater:** Leaching from landfills and sites that do not have proper waste disposal measures
- **Local water bodies:** Discharges from industrial facilities can directly release these contaminants into local water bodies, including rivers, lakes, and streams.
- **Air:** Released into the air during manufacturing activities
- **Land:** Leaching from landfills and sites that do not have proper waste disposal measures

The pathways that the contaminants can flow between the above environmental counterparts are shown in Figure 6.

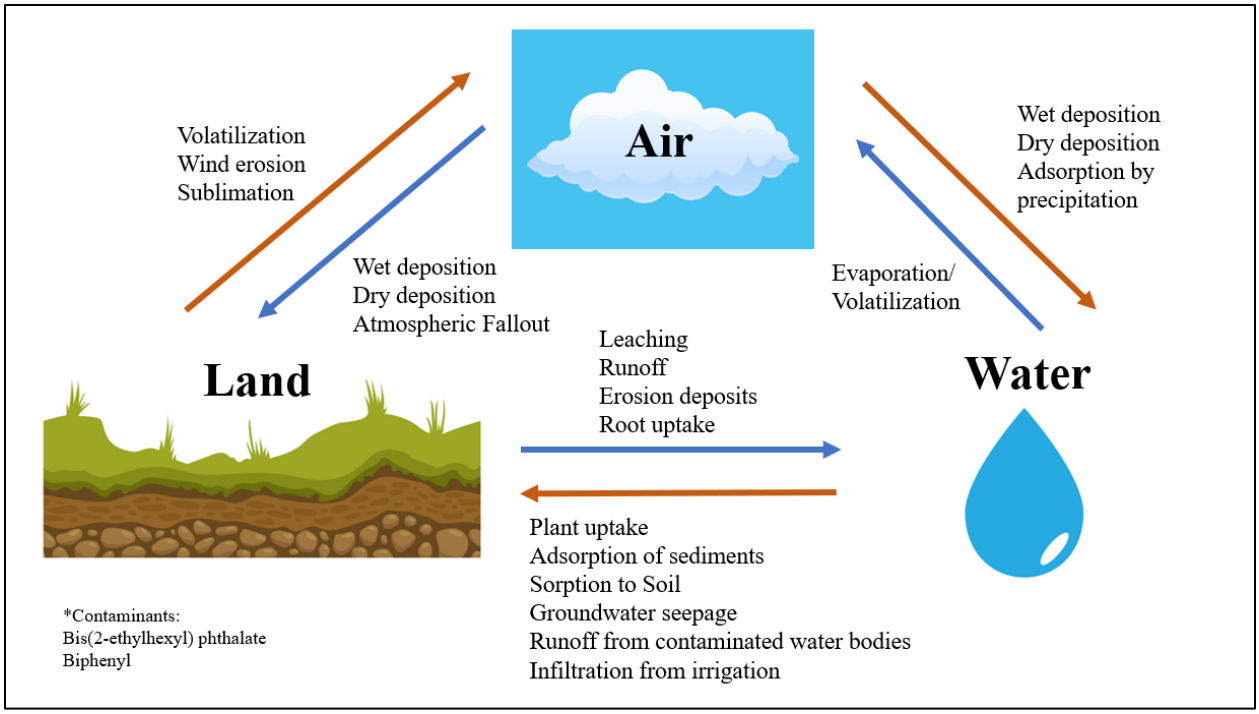

Figure 6-The contaminant transport mechanisms between air, water, and land for biphenyl and DEHP (Government of Canada, 1994)

As most of the contaminants were found in air, the pathway from air to water was explored a bit further. Contaminants in the air usually transfer to water bodies through wet (rain, snow, fog etc.) and dry (dust and gases that become acidic) deposition. Once they enter waterways directly or through surface runoff, they can be transported to other streams or bodies of water.

Aforementioned, biphenyl is currently banned in Canada, however machinery that still uses it can be used until the end of its service life. Thus, it can be assumed that most of the biphenyl air emissions are from machinery in the manufacturing plant. For example, in the synthetic fiber industry, biphenyl can be released as a volatile organic compound (VOC) in the pre-spinning process (dope preparation), and post-spinning process (washing, crimping etc.). Additionally, the spinning process can release small trace amounts in the dry and wet solvent spinning process, as well as through vaporized lubricants and oils (US EPA, 1990). For DEHP, it can be released at different stages in different industries. For example, in the rubber manufacturing industry, it can be released to the air through evaporation in the compounding, molding, shaping, and vulcanization stage (Huang et al., 2022). As all these stages contain the application of high temperature, DEHP can be released in any of the stages, depending on the industry and the regulations.

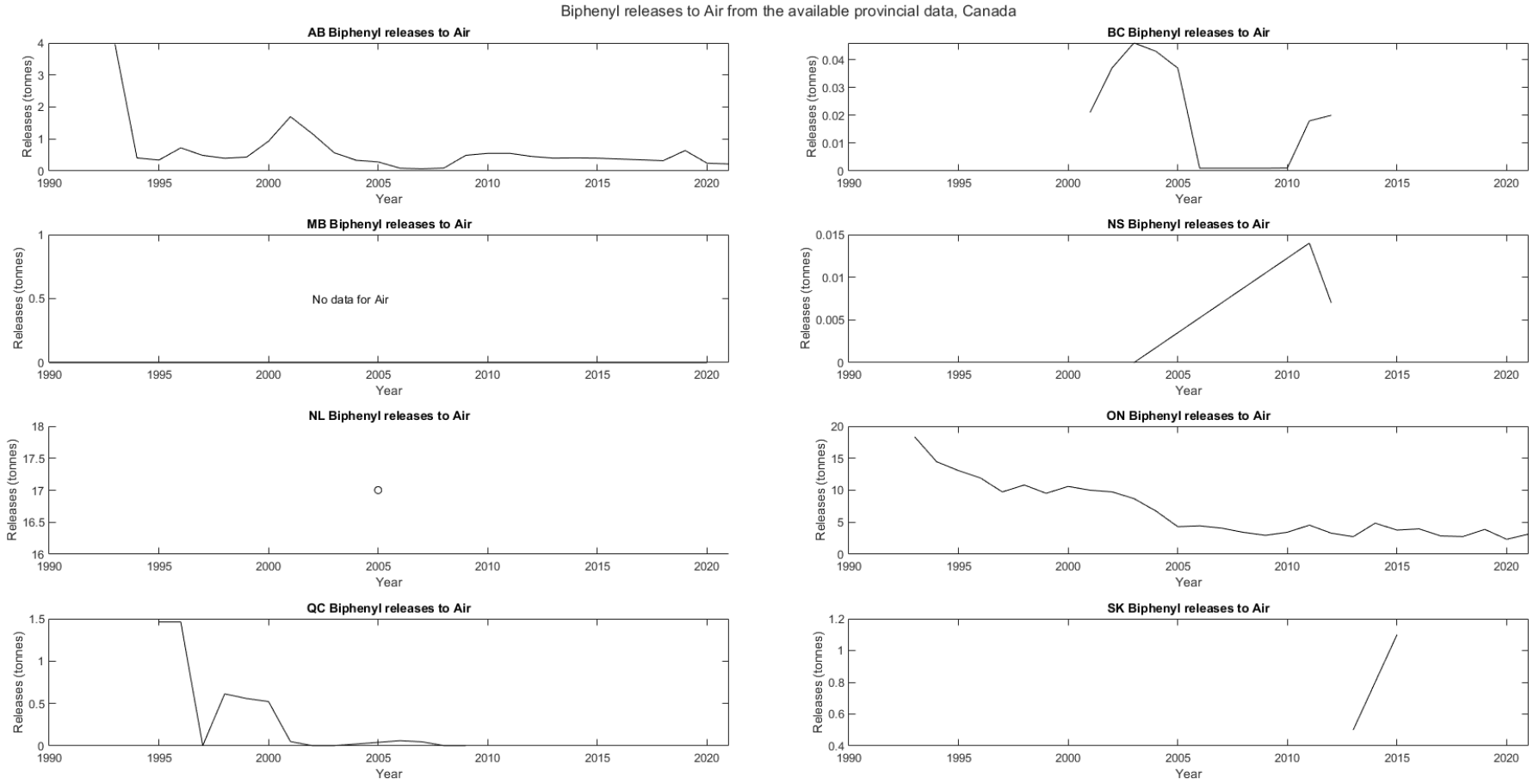

Figure 7-Biphenyl releases compared between the provinces, ejected to Air

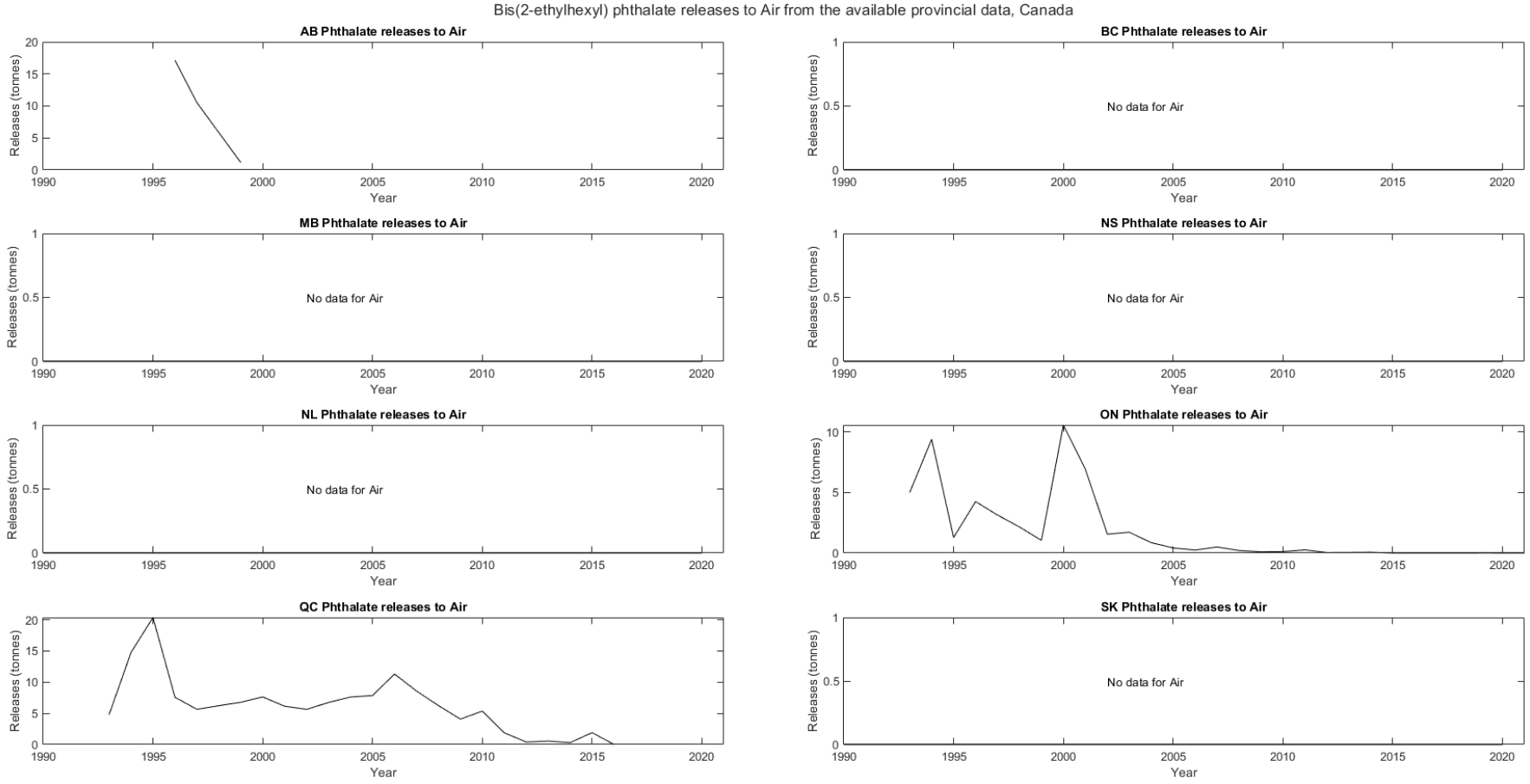

Figure 8-Bis(2-ethylhexyl) phthalate releases compared between the provinces, ejected to Air

3.4. Facility Type

3.4.1. Biphenyl

Throughout the years, many industries as shown have been contributing to the biphenyl release to different environmental compartments. All the identified industries mainly release to the air. The total release of biphenyl to the environment from 1993 till 2021 was 214.67 tonnes of 666 total incidents, and it significantly decreased in the last 10 years to reach 43.89 tonnes (77.11% decrease), making the total release between 1993 to 2010 to be almost four times higher than the total release from 2011 to 2021. Figure 9 and Figure 10 show the trends of biphenyl release over the time by the industries and indicate the timeline of each industrial contribution of the pollution.

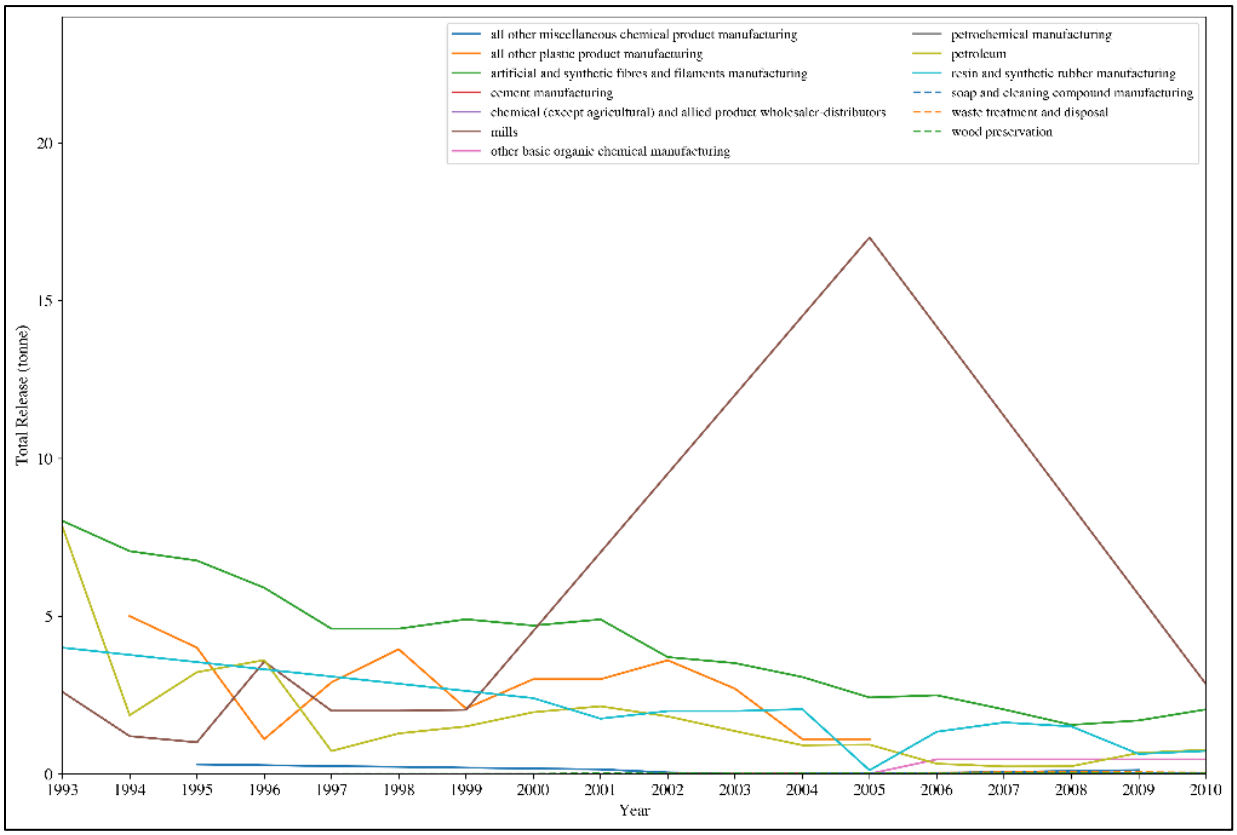

Figure 9-The total biphenyl releases among various industries from 1993 to 2010

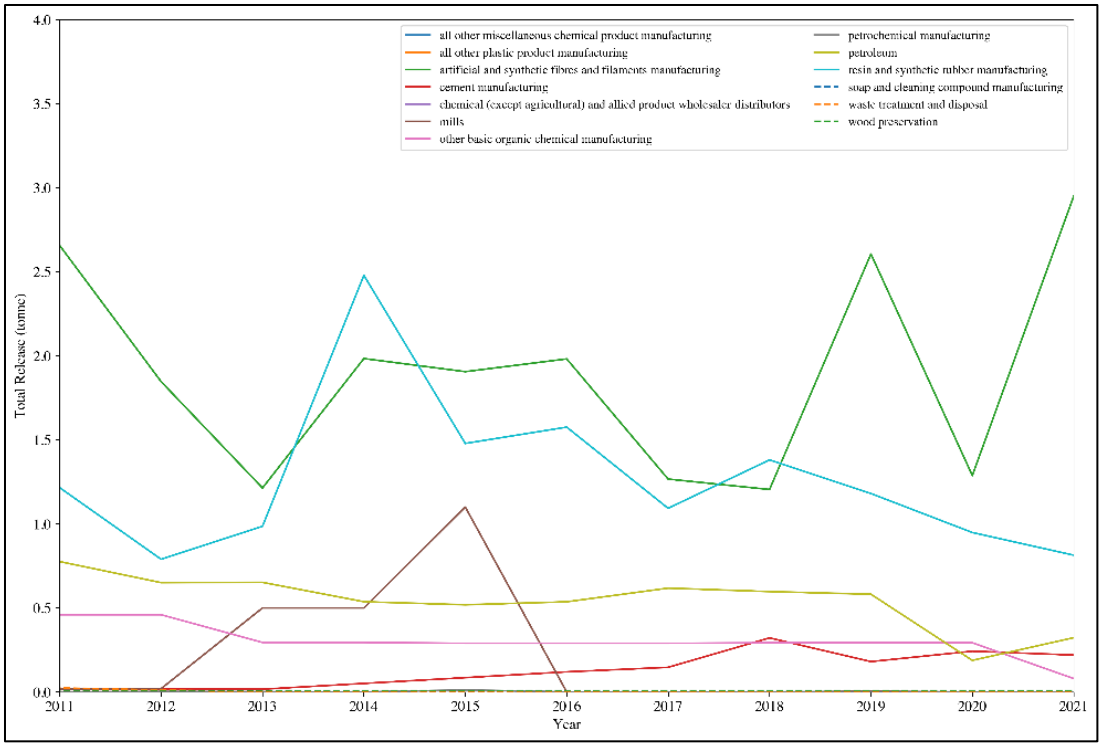

Figure 10-The total biphenyl releases among various industries from 2011 to 2021

The percentage of the pollutant released in air is 99.6% of the total release in the environment. However, the only three industries that released biphenyl in air and land are petroleum life cycle industries, yarn and fibers milling, and artificial and synthetic fibers manufacturers. However, the only industry releasing into water is the fiber manufacturers. Over the past 20 years, the highest contributing industry was artificial and synthetic fibers manufacturing with a total air release of 94.62 tonnes. However, it was reduced to reach 20.875 tonnes in the past 10 years, leading to 77.9% decrease. As shown in Figure 11, plastic products manufacturing, mills, and resin and synthetic rubber manufacturing are coming to second with ~32 tonnes of biphenyl in the air.

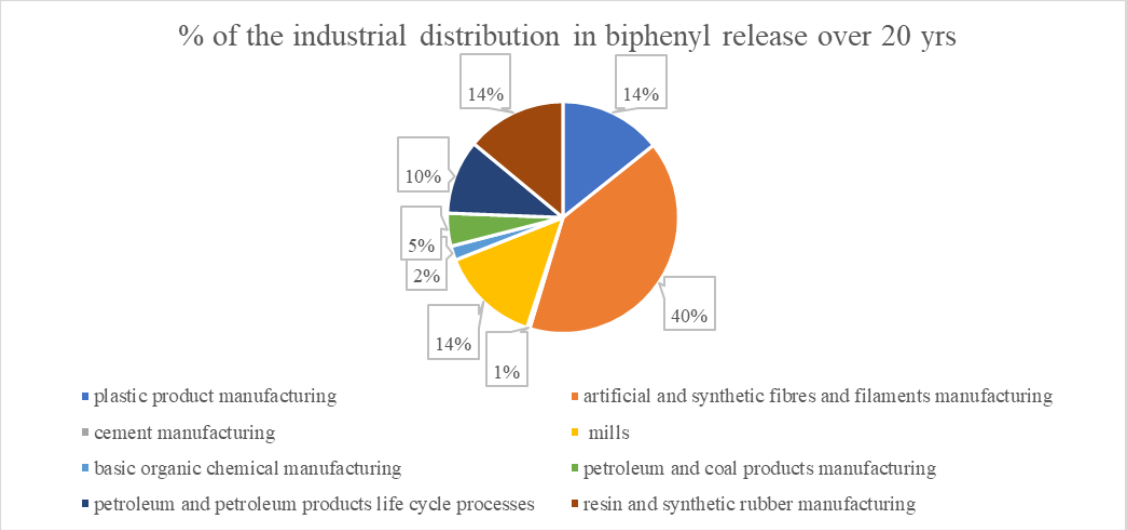

Figure 11-Industrial distribution of Biphenyl release over 20 years

There were some industries as universities, iron foundries, cement manufacturing, soap and cleaning products and wood preservation that had <2 release incidents throughout the 20 years. Table 1 demonstrates the polluting industries and categories them with their incident frequency. However, in the past 10 years, the percentage contribution to pollution has changed as many industries mitigated their release. Figure 12 shows how the contribution percentage for industries changed and how several industries stopped releasing biphenyl. The pollution from plastic products manufacturing industry has either been regulated and stopped or their data was missing. It is also shown that the biphenyl pollution from rubber industry was not reduced as much as the other industries did as it only witnessed 33.4% decrease, while the others had 70-90% reduction. Additionally, biphenyl pollution has increased in the organic chemical manufacturing industry by 53%.

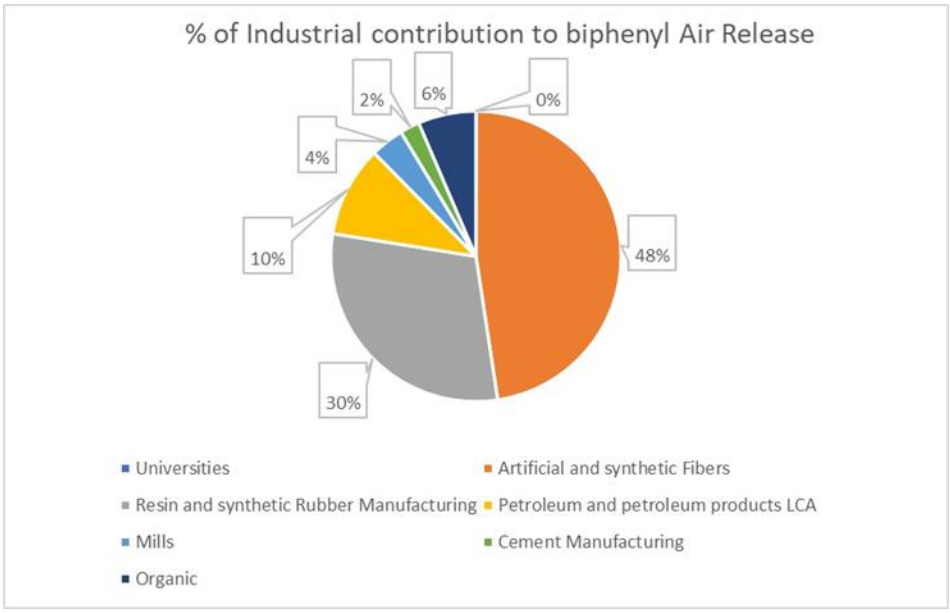

Figure 12-Industrial distribution of Biphenyl released to the air

Table 1-Biphenyl Industrial categorization and number of incidents

No.	**Industry Name**	**No. of incidents**
1	Resin and Synthetic Rubber Manufacturers	27
2	**Artificial and Synthetic Fibers and Filaments Manufacturers**	**110**
3	Cement Manufacturers	11
4	Soap and Cleaning Compound Manufacturers	7
5	Organic chemical manufacturers	34
6	Plastic products manufacturers	12
7	non-ferrous metal (except aluminum) smelting and refining	7
8	Petroleum and coal products manufacturers	42
9	**Mills**	**25**
i	Newspaper Milling	1
ii	Fibers and Yarn Milling	12
iii	Mechanical Pulp Milling	10
iv	Chemical Pulp Milling	2
10	**Petroleum Life Cycle Activities**	**334**
i	Petroleum Refineries	182
ii	Petroleum wholesalers' distributers	41
iii	Petroleum and Petroleum Products Merchant Wholesalers	82
iv	Petrochemical Product Manufacturers	29

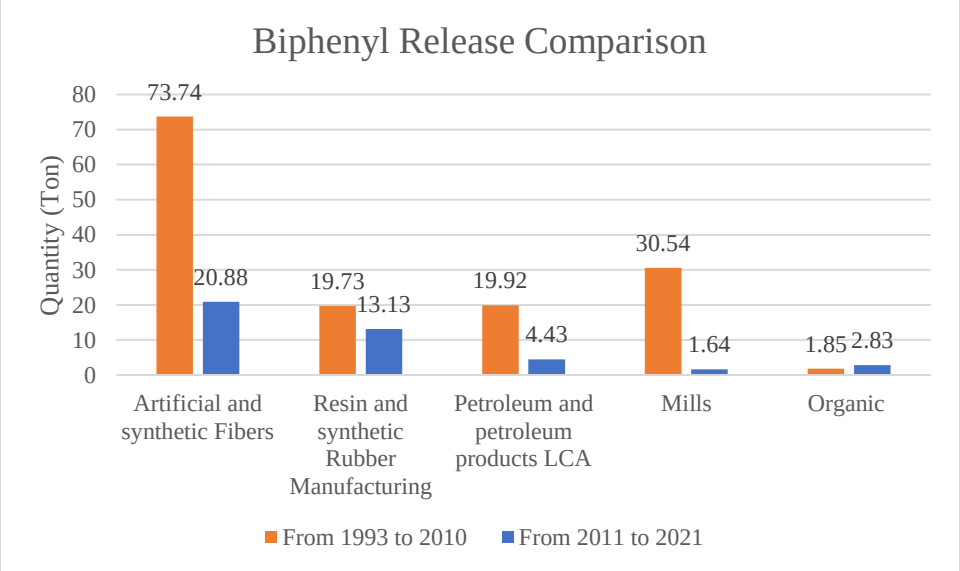

Figure 13-Biphenyl release comparison

Moreover, it is necessary to compare the number of responsible companies in each industry to understand their performance and quality control efficiency and prioritize which industries need regulations. In Figure 14, it is observed that the highest incident rate happens in companies in petroleum and petroleum product industry, where it reached 17 incidents over the past 10 years.

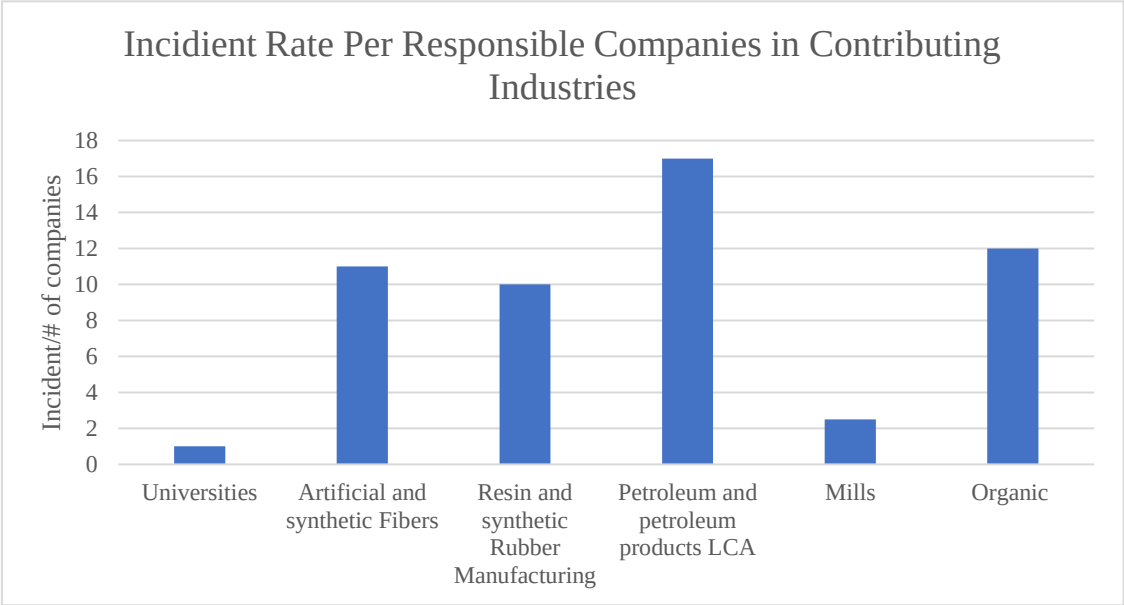

Figure 14-Incident Rate Per Responsible Companies in Contributing Industries

Additionally, the quantity of released biphenyl per incident was reviewed to understand how the incident was in each industry. The following Figure 15 indicated that the highest amount released in one incident happened in cement manufacturing industry of 3.21 tonne/incident, although it has only 11 incidents in their history with a total of 35.35 tonnes. In second, the plastic product manufacturers and mills industry, especially yarn and fiber milling, release 2.7-2.8 tonne in every incident that occurred.

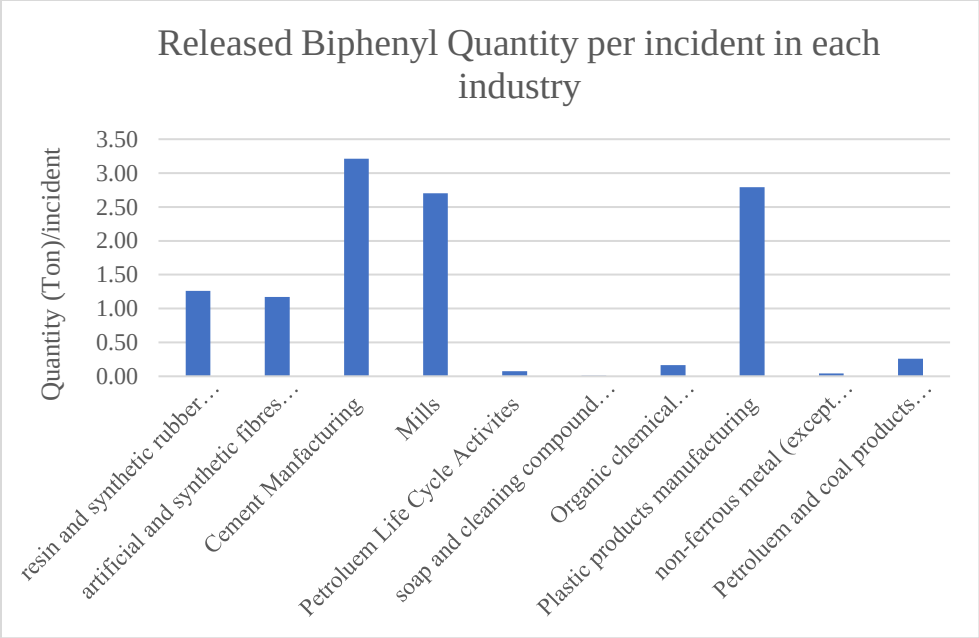

Figure 15-Released Biphenyl Quantity per incident in each industry

The spatial distribution of biphenyl pollution point sources were identified in Figure 16. The main provinces have facilities releasing biphenyl are Ontario, Alberta, Quebec, British Columbia, and Saskatchewan. The most polluted place of biphenyl is Kingston, Ontario as it hosts two facilities manufacturing artificial and synthetic fibers. These two facilities are operated by the same company and responsible for 22 incidents and 20.88 tonnes of total released biphenyl in air, land, and water bodies throughout the past 10 years.

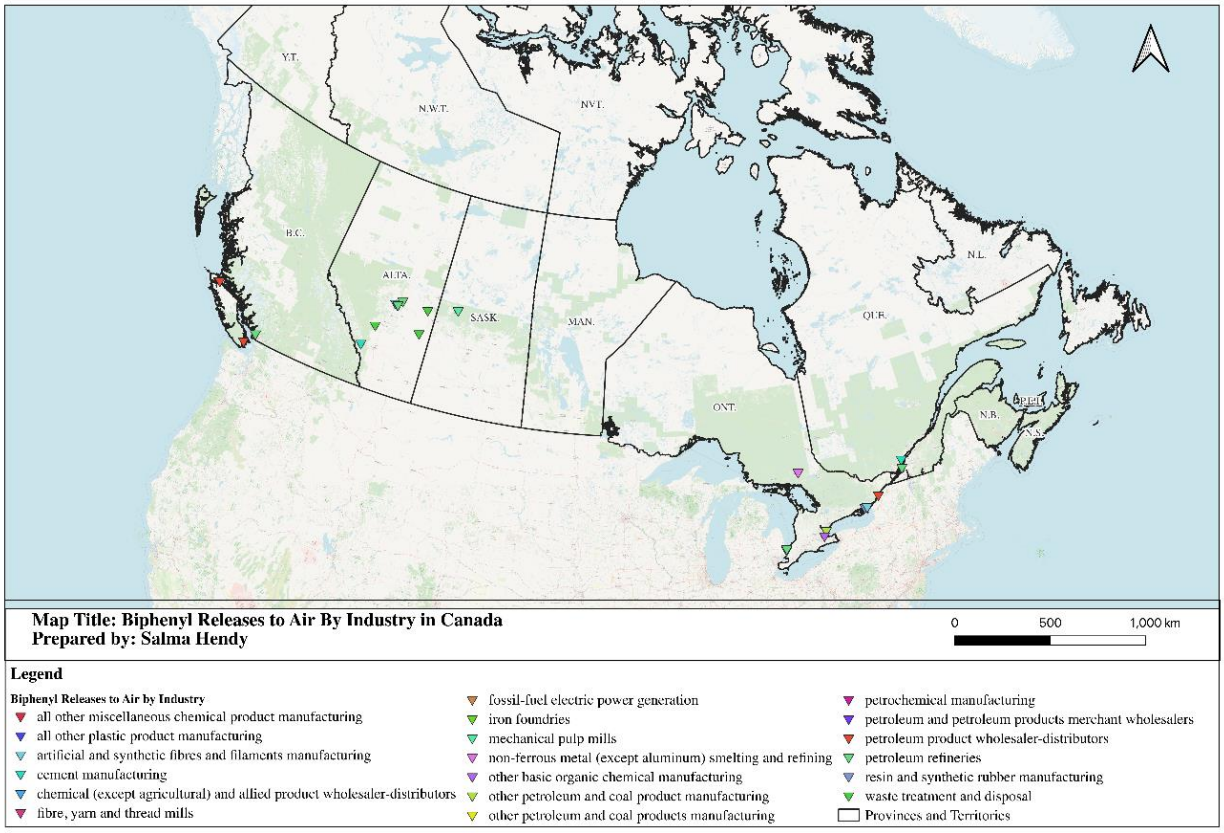

Figure 16-Spatial distribution of biphenyl pollution point sources

3.4.2. Bis(2-ethylhexyl) phthalate

There are 38 industries in Table 2 releasing phthalate in the environment. The total amount of phthalate released in the past 18 years is 245.4 tonnes, where it decreased in the last 10 years to reach 17.1 tonnes. Considering the emissions in the last 20 years, the highest industrial release is coming from rubber product manufacturing with 36% contribution to the total release, where there were 80.9 tonnes released. However, the rubber product manufacturers managed to significantly lower the total releases in the last 10 years to reach 0.743 tonnes. Figure 17 and Figure 18 illustrate the trends of phthalate release over the time by the industries and indicate the timeline of each industrial contribution of the pollution.

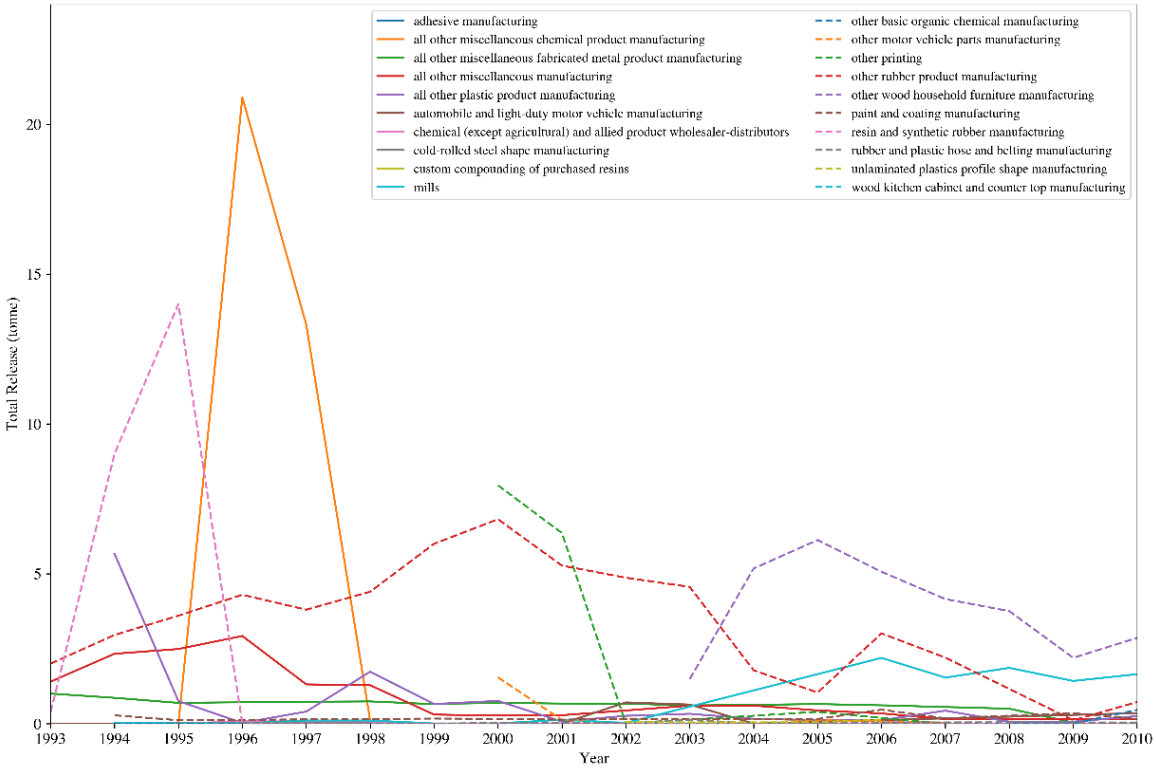

Figure 17-The total phthalates releases among various industries from 1993 to 2010

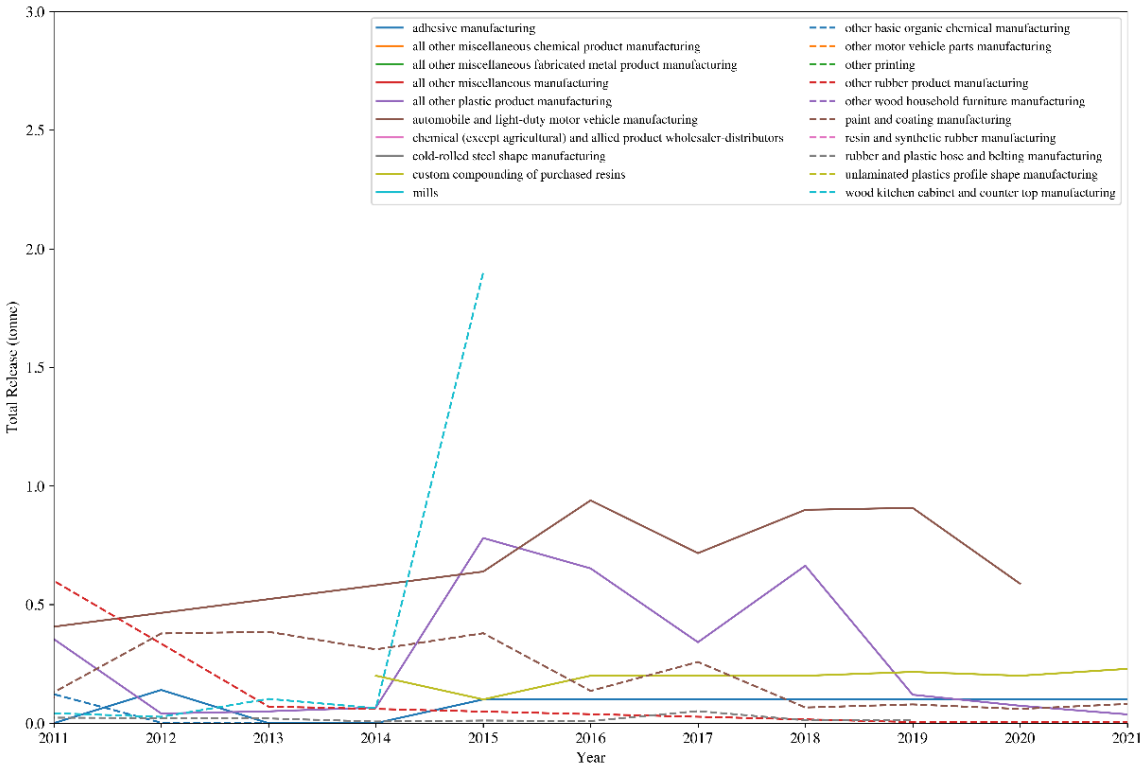

Figure 18-The total phthalates releases among various industries from 2011 to 2021

As observed from Figure 19, wood and chemical products manufacturers were the second industries releasing phthalates with 15% of the total releases. Most of the releases were in the air (~90%), and the others were in land. There was no record for phthalates release in water bodies. It is worth mentioning that most of the incidents in different industries had total releases in all media less than 1 tonne.

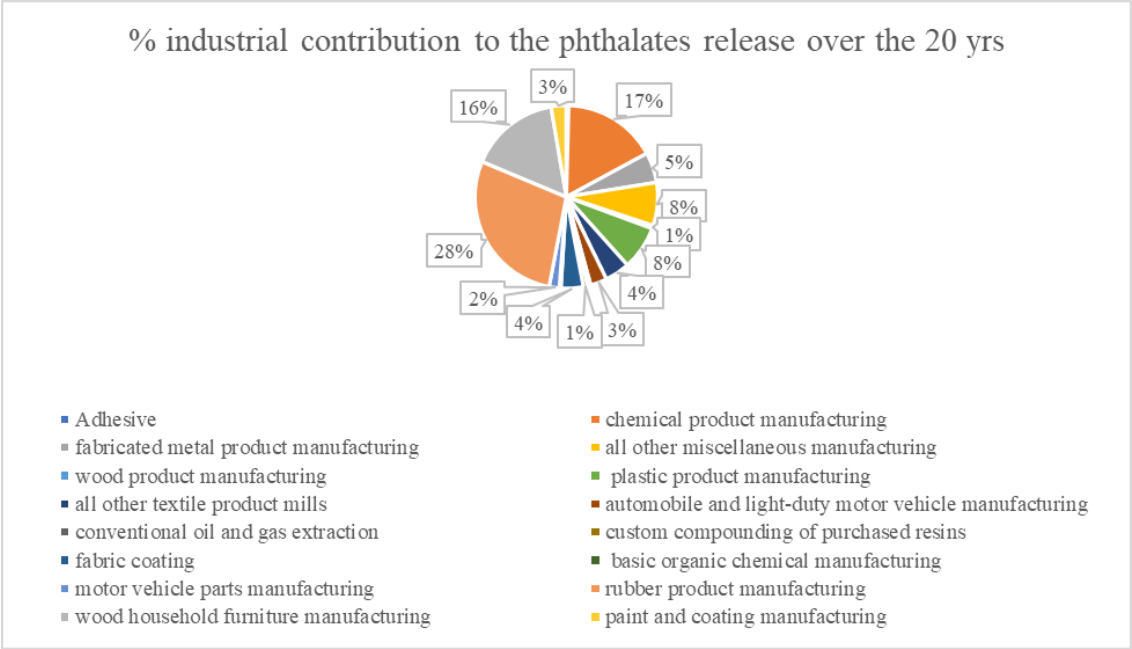

Figure 19-Industrial distribution of Phthalate release over 20 years

In Figure 20, it is indicated that many industries have stopped releasing phthalates in the past 10 years as oil and gas extraction, motor vehicle parts manufacturing, printing, textile product milling, and urethane and foam products manufacturing.

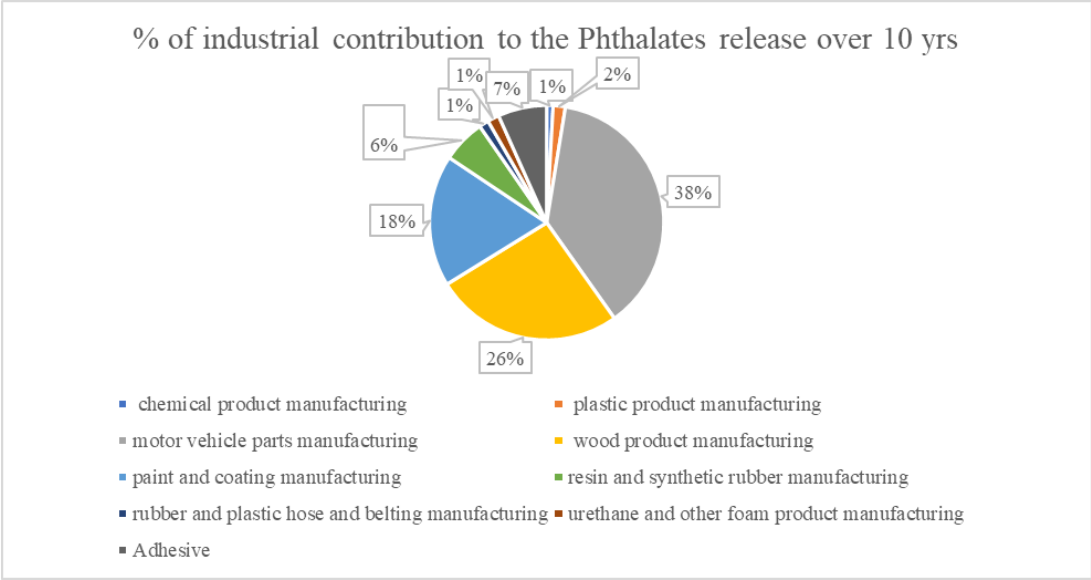

Figure 20-Industrial distribution of Phthalate released to the air

Comparing the quantity released from each industry between 1993 to 2010 and between 2011 to 2021, it is also shown that the phthalate pollution from motor vehicle parts manufacturing and adhesive industry have only occurred incidents in the last 10 years. The different releasing industries have various decreasing rates, not as the biphenyl polluting industries. As seen in Figure 21, the average decreasing ratio among the releasing industries is 98-99%, however, rubber and plastic hoses, and paint and coating manufacturers have 73% and 59% decrease in their releases respectively.

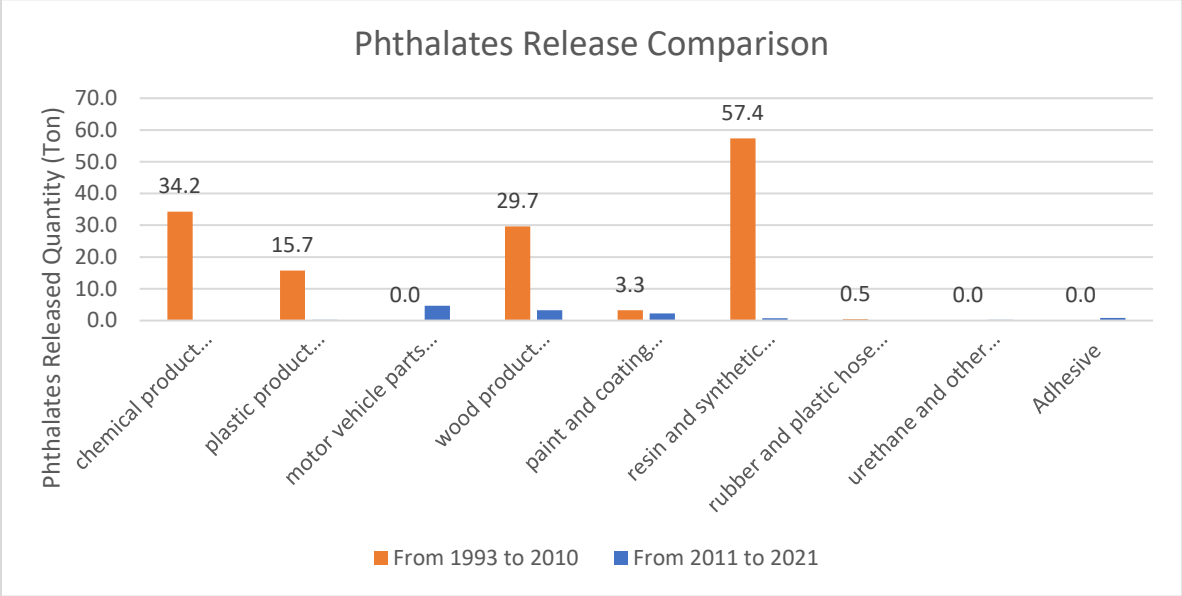

Figure 21-Phthalates Release Comparison

To assess each industry's performance and effectiveness in quality control and to determine which sectors require restrictions in order of importance, it is also vital to compare the number of responsible businesses in each sector. Table 2 shows that, during the last 20 years, companies in the plastic product industry have seen the greatest occurrence rate, with 135 release events. The second most frequent industry having incidents are resin and synthetic rubber manufacturing.

Table 2-Phthalate Industrial categorization and number of incidents

No.	**Industry Type**	**No. of Incidents**
1	chemical product manufacturing	7
2	rubber and plastic hose and belting manufacturing	42
3	**motor vehicle parts manufacturing**	**40**
i	automobile and light-duty motor vehicle manufacturing	30
ii	motor vehicle plastic parts manufacturing	4
iii	other motor vehicle parts manufacturing	6
4	**wood product manufacturing**	**29**

No.	**Industry Type**	**No. of Incidents**
i	all other miscellaneous wood product manufacturing	1
ii	other wood household furniture manufacturing	23
iii	wood kitchen cabinet and countertop manufacturing	5
5	paint and coating manufacturing	49
6	**resin and synthetic rubber manufacturing**	**103**
i	other rubber product manufacturing	40
ii	resin and synthetic rubber manufacturing	63
7	urethane and other foam product manufacturing	1
8	Adhesive	19
9	**Plastic product manufacturing**	**135**
i	all other plastic product manufacturing	119
ii	plastic film and sheet manufacturing	2
iii	unlaminated plastic profile shape manufacturing	9
iv	unsupported plastic bag manufacturing	1
v	unsupported plastic profile shape manufacturing	4

Figure 22 shows the quantified DEHP incident release in each industry, and it excludes the highest industry with releasing quantity per incident. The most industry releasing phthalate per incident is chemical product manufacturing with 4.9 tonnes in each incident; however, there were only 7 incidents in their history. Wood product manufacturers come in second with 1.13 tonnes/incident with 29 events.

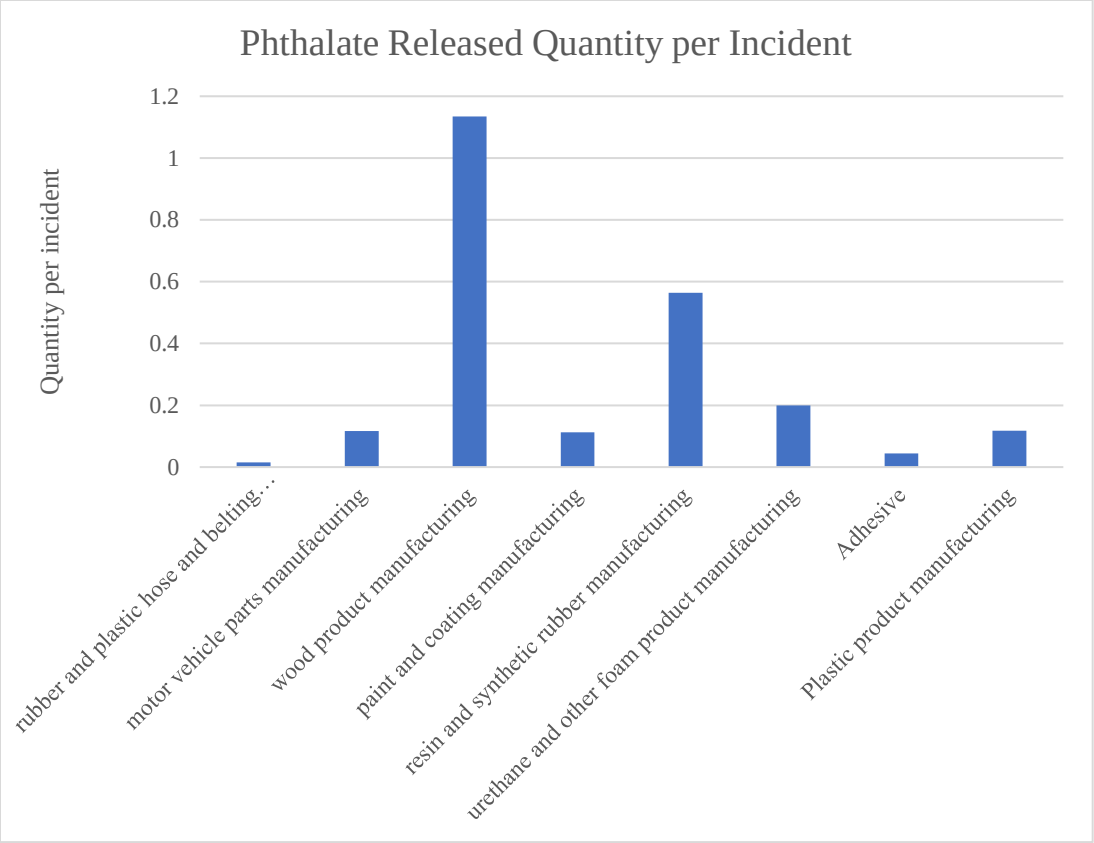

Figure 22-Phthalate Released Quantity per Incident

The spatial distribution of phthalate pollution point sources were identified in Figure 23. The main provinces that have facilities releasing phthalate are Ontario and Quebec. Alberta had only one release event of 17.12 tonnes in Calgary which was the highest release incident occurred; however, it was excluded in our spatial representation. The second polluted location is in Sherbooke, Quebec as there were one of highest release across Canada with 23 tonnes, happening in the same company. Also, Toronto witnessed phthalate release of 10.5 tonnes.

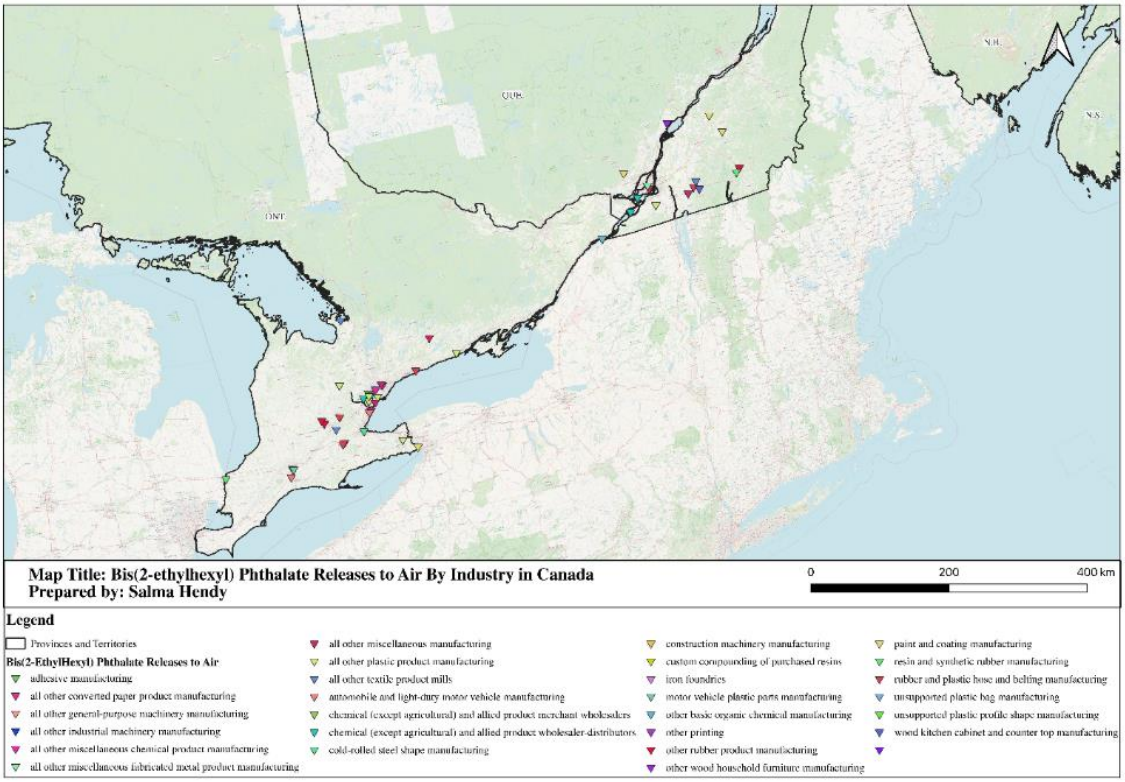

Figure 23-Spatial distribution of Phthalate pollution point sources

3.5. *Phthalate (DEHP) and Plastic*

Phthalates have been found all over the place, but little is understood about the regulating mass transfer mechanism and the kinetics of leaching into aquatic systems. Henkel et al. (2022) introduced a leaching rate time dependent curves for 3 phthalic acid esters, including di(2-ethylhexyl) phthalate. The curve consists of six different PVC microplastics. In the most conservative approach, we will take the highest leaching rate PVC microplastic type after 120 days. The released phthalate mass leached from each PVC microplastic is 14.2 µg. In our analysis to quantify the released number of phthalates in the environment, the total release of phthalates in the last 20 years was 245.4 tonnes, and 17.1 tonnes in the last 10 years. We assumed that the final fate of all the released phthalates will end up in the water bodies; therefore, the released amount of phthalates would be 1.728×10^{13} microplastics. If we only consider the last 10 years total release, the phthalates quantity would be 1.204×10^{12} microplastics. The following table demonstrates the equivalent amount of microplastics that the phthalate leached from to the environment.

Table 3-Amount of Phthalate and microplastics released

Year	Total released Quantity (tonne)	Released Microplastic
2021	0.451	3.18E+10
2020	1.0257	7.22E+10
2019	1.439	1.01E+11
2018	1.941	1.37E+11
2017	1.669	1.18E+11

3.6. *Based on the Facility Prevention/Treatment Activities, Prediction of the Burdens*

For this purpose, first-degree polynomial trendlines are added to each of the provincial time-series. There could be higher order polynomial predictors with more accurate outputs, however, it is not robust to add a n-order polynomial to (n + 1) data points as the line (or curve) will exactly pass through the points, which is not a good predictor model. Moreover, in this study, the focus is to see whether the prevention activities have had any positive results or not, rather than comparing various models' output and performance. Hence, using "polyfit" and "polyval" functions in MATLAB, trendlines, constant coefficient values, and ordinary coefficient of determination (R^2) are created and exported for each of the graphs shown in Figure 24 and Figure 25.

For biphenyl, Alberta, British Columbia, Ontario, and Saskatchewan time-series show decreasing trendlines in the last 10 years of study (2011-2021) as shown in Figure 24, however, R^2 do not exceed 50%; being equal to 0.058, 0.44, 0.043, and 0.44 respectively. This represents a wide difference and intense fluctuation between yearly released data in some of the provinces. Additionally, Manitoba, with only 3 datapoints, and Quebec results indicated an upward behavior of biphenyl ejections to the environment with the coefficient of determination of about 0.90 and 0.58. For Nova Scotia and Newfoundland and Labrador, no sufficient data was available for a trendline analysis, so, their results are not reliable.

Also, DEHP diagrams in Figure 25 indicate insignificant downward tendency in Quebec with roughly $R^2 = 0.14$ while the opposite behavior could be noticed from Ontario data ($R^2 = 0.07$). Moreover, based on the trendline equations derived from provincial time-series data points, we could be able to model the burden of biphenyl and DEHP in the coming years.

Finally, the combination of low R^2 values and the first constant coefficient for the line equation (which is the coefficient multiplied by time as the independent parameter in this case) shown in the Figure 24 and Figure 25 means approximate constant release of 1 tonne biphenyl in Alberta and Ontario and 1 tonne and 2 tonnes of DEHP in Ontario and Quebec respectively.

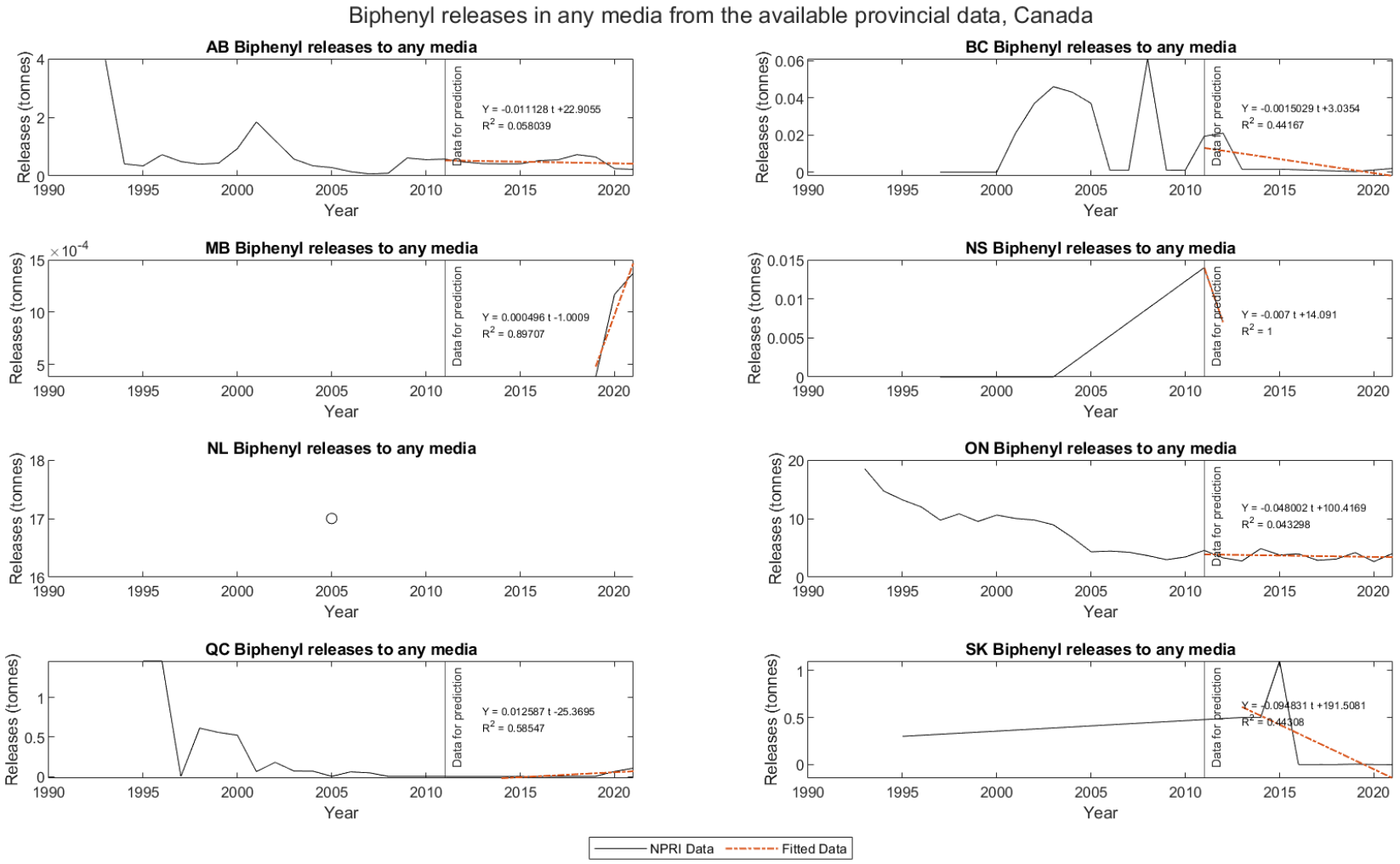

Figure 24-Biphenyl predictions in each province

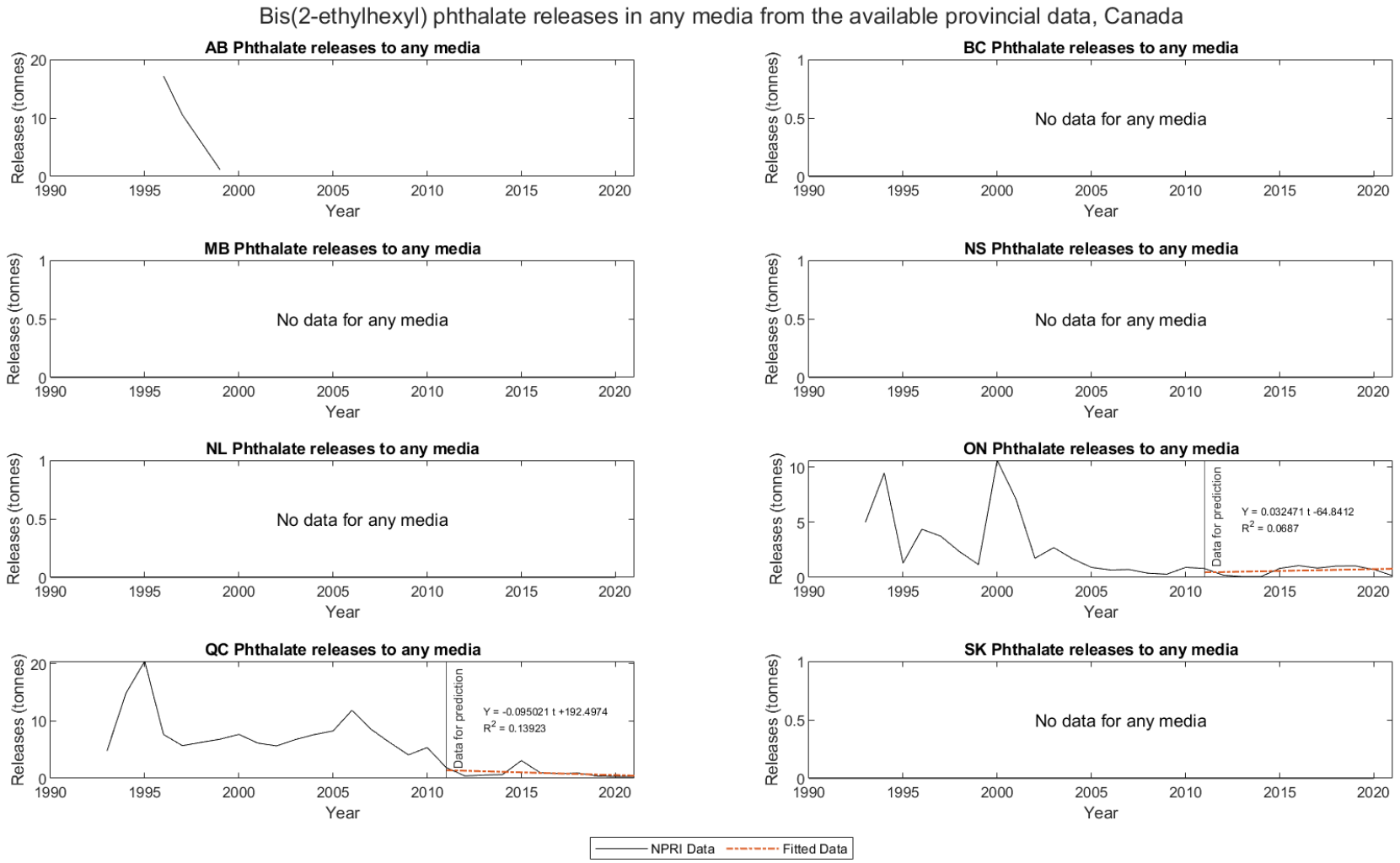

Figure 25-Phthalate predictions in each province

Similarly, Sun et al. have resulted in a declining behavior (Figure 26) measuring long term trend of temperature-corrected total polychlorinated biphenyl (PCB) concentrations (partial pressures in the gas phase).

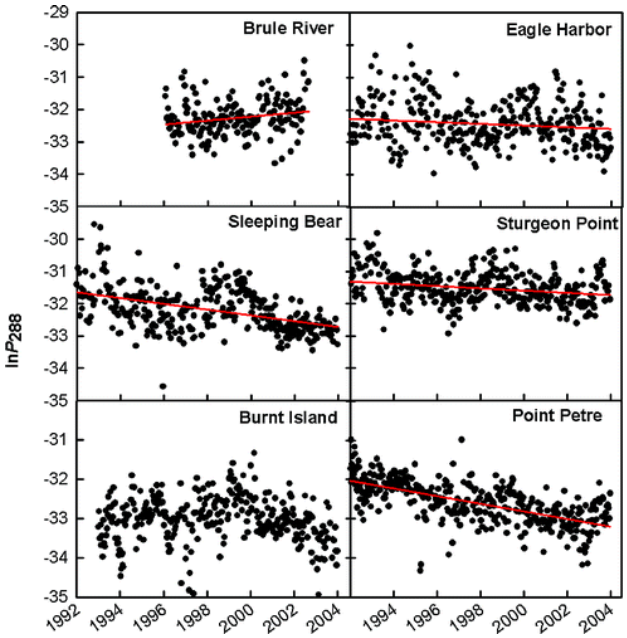

Figure 26-Long-term variations of PCB in partial pressure phase measured by Sun et al.

This analysis is conducted through several atmospheric temperature corrections to diminish the effect of secondary parameters on gas-phase PCBs using Clausius-Clapeyron equation which generates modified partial pressure P_{288} , conversion of gas-phase PCB concentration to partial pressure. They have indicated this downward tendency at 4 out of 6 regionally representatives, including Eagle Harbor, Sleeping Bear, Sturgeon Point, and Point Petre which could be seen in the Figure 27

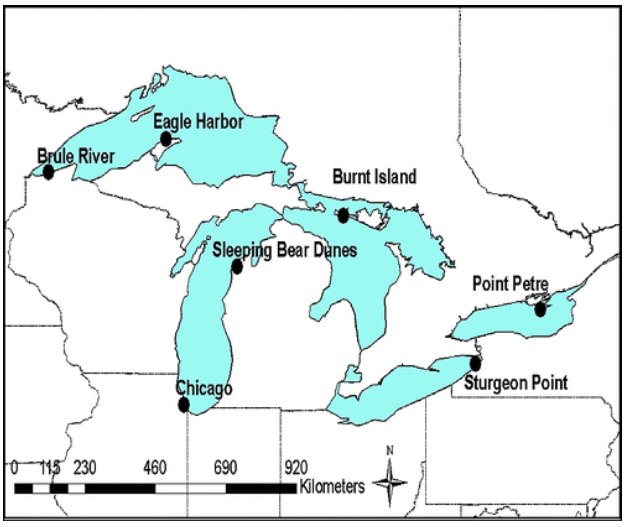

Figure 27-Measuring points in the study

This validates the results for the corresponding data points and time-series as the northern sections of these representatives are all in the Canada's boundary. Besides, there is an increasing behavior for Brule River. This source point is in Wisconsin, USA, that is not within our region of interest (Sun et al., 2007).

Also, for DEHP, there was no related literature mentioning similar results in terms of time series alterations of the releases to the environment.

3.7. The Efficiency of the Prevention and Treatment Based on the Facility Activities

As there are respective laws and regulations in place for both biphenyl and DEHP, it can be aided in the decrease of these contaminants within our environmental systems. While the chemicals may be regulated on a provincial level and a federal level, there was an absence of data from how the facilities followed these regulations.

4. Limitations and Future Directions

One of the primary constraints in this study is the lack of information recorded in the NPRI dataset. Although there are a vast number of observations and features related to various compounds being released in the environment, those for biphenyl and DEHP, it did not result in a detailed time-series. This limitation got exacerbated when the analysis dived into different environmental compartment objective. In other words, there is no valuable data for some media like water bodies, which was the main focus of this study and analysis. Furthermore, no separation between surface water bodies and groundwater bodies is conducted in the dataset, which makes it difficult to analyze the fate of our desired compounds in a more advanced approach. Moreover, there could have been a more-detailed categorization between different environmental compartments in the fourth category of data, which means the portions of pollutant being ejected to air, land, and water bodies. In addition, as the number of data points for 5 to 10 years of data is not convincing, trendlines may not result in greatly precise results for modeling the burden of contaminants in the environment.

5. Conclusion

In this study, biphenyl and bis(2-ethylhexyl) phthalate compounds were analyzed based on the NPRI datasets. Time-series data analysis of releases showed majorly downward trends of pollution in different provinces across Canada in terms of quantity and percentage. Regional analysis of the locations in which the pollutants have been ejected was conducted for each of the provinces indicating which divisions of the provinces hold the main responsibility of releases. Furthermore, the portion of compounds entering each of the environmental compartments indicated that the contaminant releases are dominated in the air media in comparison to water bodies and land sites. This led to the exploration of how the contaminants migrated between each environmental media.

Additionally, a first-degree polynomial trendline was developed and implemented to fit the 5-10 years of data for the future burdens of desired contaminants in the environment, showing downward, upward, and negligible changes of quantities released throughout the study period based on each of the provinces, however, not demonstrating accurate results based on the coefficient of determination, the only statistical indicator which was utilized in the study. Moreover, the analysis of various facilities contributing to the pollution of biphenyl and DEHP was completed in detailed to show what companies are considered in the NPRI database.

Overall, with biphenyl and bis(2-ethylhexyl) phthalate being regulated in Canada, it has led to the decrease of these contaminants with time, but more monitoring of facilities is required to obtain a conclusive result. We recommend that the federal and provincial government investigate further into the releases of facilities and consumer products to understand how these contaminants are still having a negative effect on our health and environment.

References

Beyer, A., & Biziuk, M. (2009). Environmental Fate and Global Distribution of Polychlorinated Biphenyls (pp. 137–158). https://doi.org/10.1007/978-1-4419-0032-6_5

Buha Djordjevic, A., Antonijevic, E., Curcic, M., Milovanovic, V., & Antonijevic, B. (2020). Endocrine-disrupting mechanisms of polychlorinated biphenyls. Current Opinion in Toxicology, 19, 42–49. https://doi.org/10.1016/j.cotox.2019.10.006

Canada. 2000. Canadian Environmental Protection Act, 1999: Persistence and Bioaccumulation Regulations [PDF], P.C. 2000-348, 23 March 2000, SOR/2000-107.

Canada. 2010. Department of Health. Phthalates Regulations [PDF].

Canadian Environmental Protection Act, 1999, SC 1999, c 33

Erickson, M. D., & Kaley, R. G. (2011). Applications of polychlorinated biphenyls. Environmental Science and Pollution Research, 18(2), 135–151. https://doi.org/10.1007/s11356-010-0392-1

Government of Canada. (1994). Retrieved from https://www.canada.ca/content/dam/hc-sc/migration/hc-sc/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/contaminants/psl1-lsp1/bis_2/bis_2_ethylhexyl_phthalate-eng.pdf

Government of Canada (2017). *Toxic substances list: PCBs.* Retrieved from the Government of Canada https://www.canada.ca/en/environment-climate-change/services/management-toxic-substances/list-canadian-environmental-protection-act/polychlorinated-biphenyls.html

Government of Canada (1994). Priority Substances List Assessment Report: Bis(2-ethylhexyl) Phthalate. Retrieved from the Government of Canada https://www.canada.ca/content/dam/hc-sc/migration/hc-sc/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/contaminants/psl1-lsp1/bis_2/bis_2_ethylhexyl_phthalate-eng.pdf ****

Government of Canada (2023). Risk management approach for 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP). Retrieved from the Government of Canada https://www.canada.ca/en/environment-climate-change/services/evaluating-existing-substances/risk-management-approach-1-2-benzenedicarboxylic-acid-bis-2-ethylhexyl-ester-dehp.html

Government of Canada (2013). Toxic substances list: polybrominated biphenyls. Retrieved from the Government of Canada https://www.canada.ca/en/environment-climate-change/services/management-toxic-substances/list-canadian-environmental-protection-act/polybrominated-biphenyls.html

Government of Canada (2006). PCBs. Retrieved from the Government of Canada https://www.canada.ca/en/health-canada/services/healthy-living/your-health/environment/pcbs.htmlGovernment of Canada (2017). Toxic substances list: PCBs.

Retrieved from the Government of Canada https://www.canada.ca/en/environment-climate-change/services/management-toxic-substances/list-canadian-environmental-protection-act/polychlorinated-biphenyls.html

Government of Canada. Canada.ca. (2021, August 11). https://www.canada.ca/en/environment-climate-change/services/national-pollutant-release-inventory/about-national-pollutant-release-inventory.html

Government of Canada, S. C. (2023). Annual survey of manufacturing industries, 2021. Retrieved from https://www150.statcan.gc.ca/n1/daily-quotidien/230214/dq230214a-eng.htm

Government of Canada (2020). Phthalates. Retrieved from the Government of Canada https://www.canada.ca/en/health-canada/services/chemicals-product-safety/phthalates.html

Henkel, C., Hüffer, T., & Hofmann, T. (2022). Polyvinyl Chloride Microplastics Leach Phthalates into the Aquatic Environment over Decades. Environmental Science & Technology, 56(20), 14507–14516. https://doi.org/10.1021/acs.est.2c05108

Huang, H., Wang, Z., Dai, C., Guo, J., & Zhang, X. (2022). Volatile organic compounds emission in the rubber products manufacturing processes. *Environmental Research, 212,* 113485. https://doi.org/10.1016/j.envres.2022.113485

Johnson, G. W., Quensen, I. J. F., Chiarenzelli, J. R., & Hamilton, M. C. (1964). Polychlorinated Biphenyls. In Environmental Forensics (pp. 187–225). Elsevier. https://doi.org/10.1016/B978-012507751-4/50032-X

Koch, H. M., Preuss, R., & Angerer, J. (2006). Di(2-ethylhexyl)phthalate (DEHP): human metabolism and internal exposure – an update and latest results 1. International Journal of Andrology, 29(1), 155–165. https://doi.org/10.1111/j.1365-2605.2005.00607.x

Li, Y.-F., Harner, T., Liu, L., Zhang, Z., Ren, N.-Q., Jia, H., Ma, J., & Sverko, E. (2010). Polychlorinated Biphenyls in Global Air and Surface Soil: Distributions, Air−Soil Exchange, and Fractionation Effect. Environmental Science & Technology, 44(8), 2784–2790. https://doi.org/10.1021/es901871e

Li, Z., Hogan, K. A., Cai, C., & Rieth, S. (2016). Human Health Effects of Biphenyl: Key Findings and Scientific Issues. Environmental Health Perspectives, 124(6), 703–712. https://doi.org/10.1289/ehp.1509730

Meek, M. E., & Chan, P. K. L. (1994). Bis(2-ethylhexyl)phthalate: Evaluation of risks to health from environmental exposure in Canada. Journal of Environmental Science and Health, Part C, 12(2), 179–194. https://doi.org/10.1080/10590509409373439

Rowdhwal, S. S. S., & Chen, J. (2018b). Toxic Effects of Di-2-ethylhexyl Phthalate: An Overview. BioMed Research International, 2018, 1–10. https://doi.org/10.1155/2018/1750368

Statistics Canada. (2023, February 14). *Annual survey of manufacturing industries, 2021*. https://www150.statcan.gc.ca/n1/daily-quotidien/230214/dq230214a-eng.htm

Sun, P., Basu, I., Blanchard, P., Brice, K. A., & Hites, R. A. (2007). Temporal and spatial trends of atmospheric polychlorinated biphenyl concentrations near the Great Lakes. *Environmental Science & Technology*, *41*(4), 1131–1136. https://doi.org/10.1021/es061116j

US EPA (1990). Organic Chemical Process Industry, Organic Chemical Process Industry: 6.9 Synthetic Fibers 6.9-1-6.9-17.

Zarean, M., Keikha, M., Poursafa, P., Khalighinejad, P., Amin, M., & Kelishadi, R. (2016). A systematic review on the adverse health effects of di-2-ethylhexyl phthalate. Environmental Science and Pollution Research, 23(24), 24642–24693. https://doi.org/10.1007/s11356-016-7648-3

Appendix

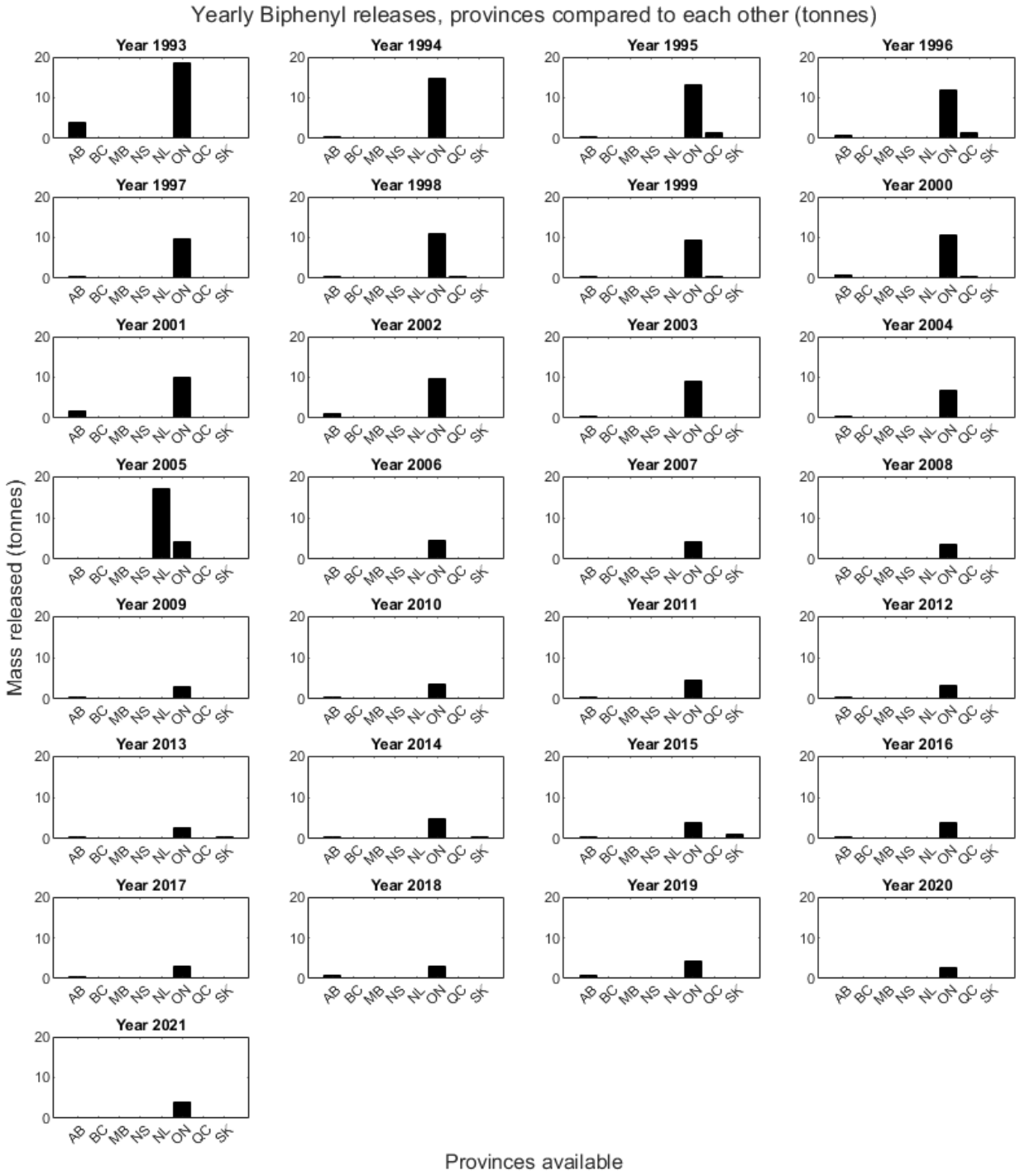

Figure 28- Quantities of Biphenyl released in total in each of the provinces

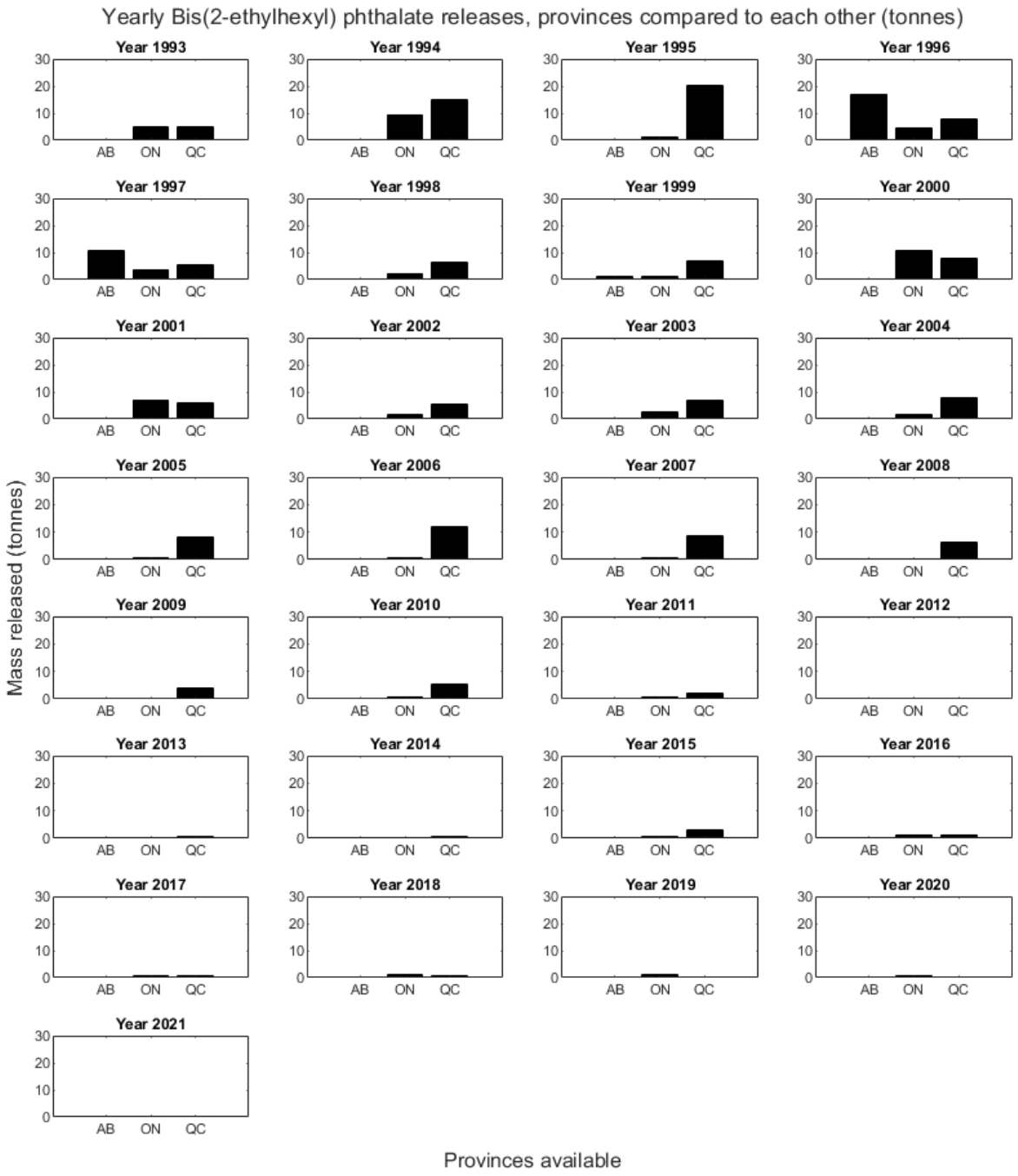

Figure 29- Quantities of Phthalate released in total in each of the provinces

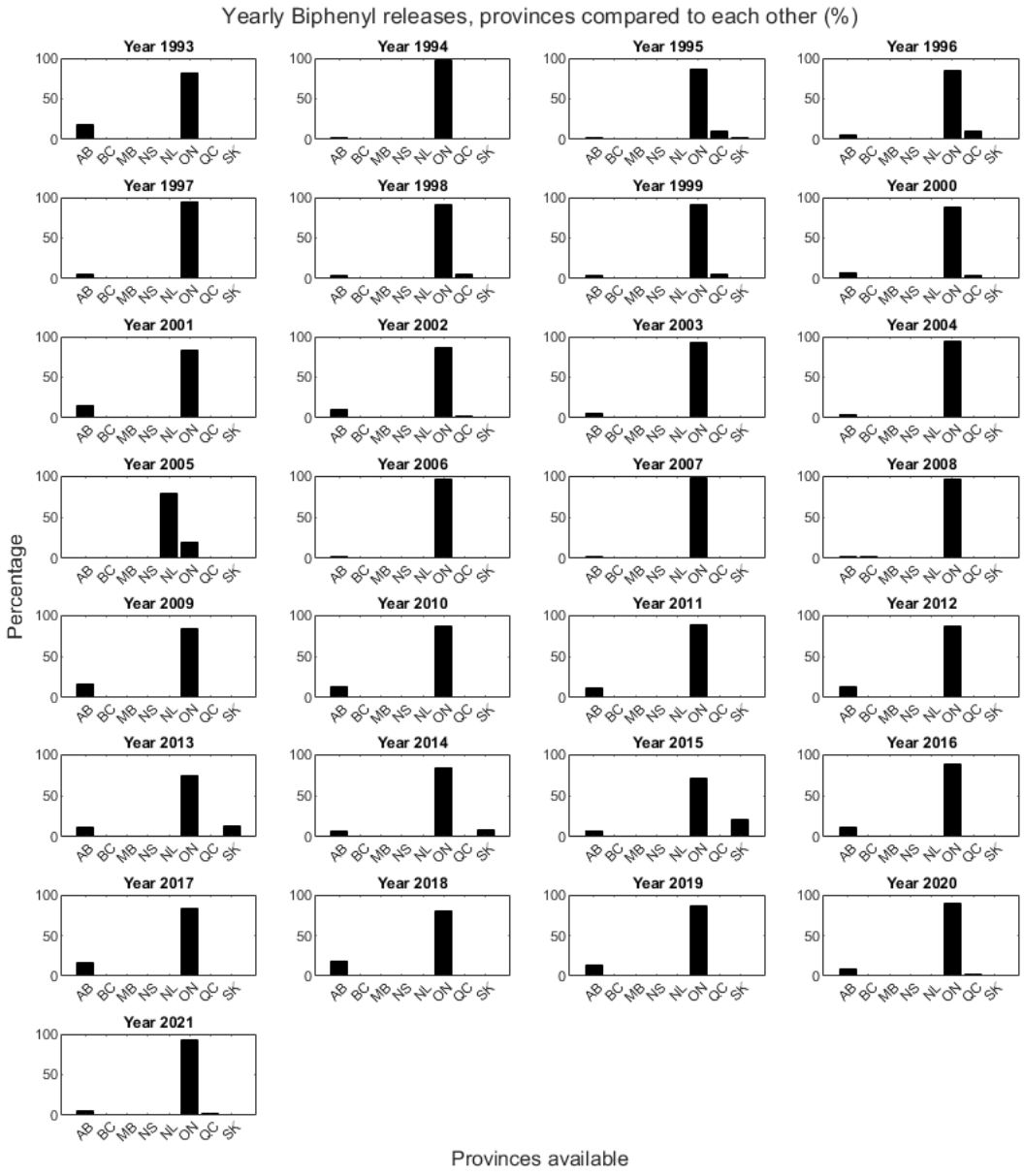

Figure 30- Percentage of Biphenyl released in total in each of the provinces

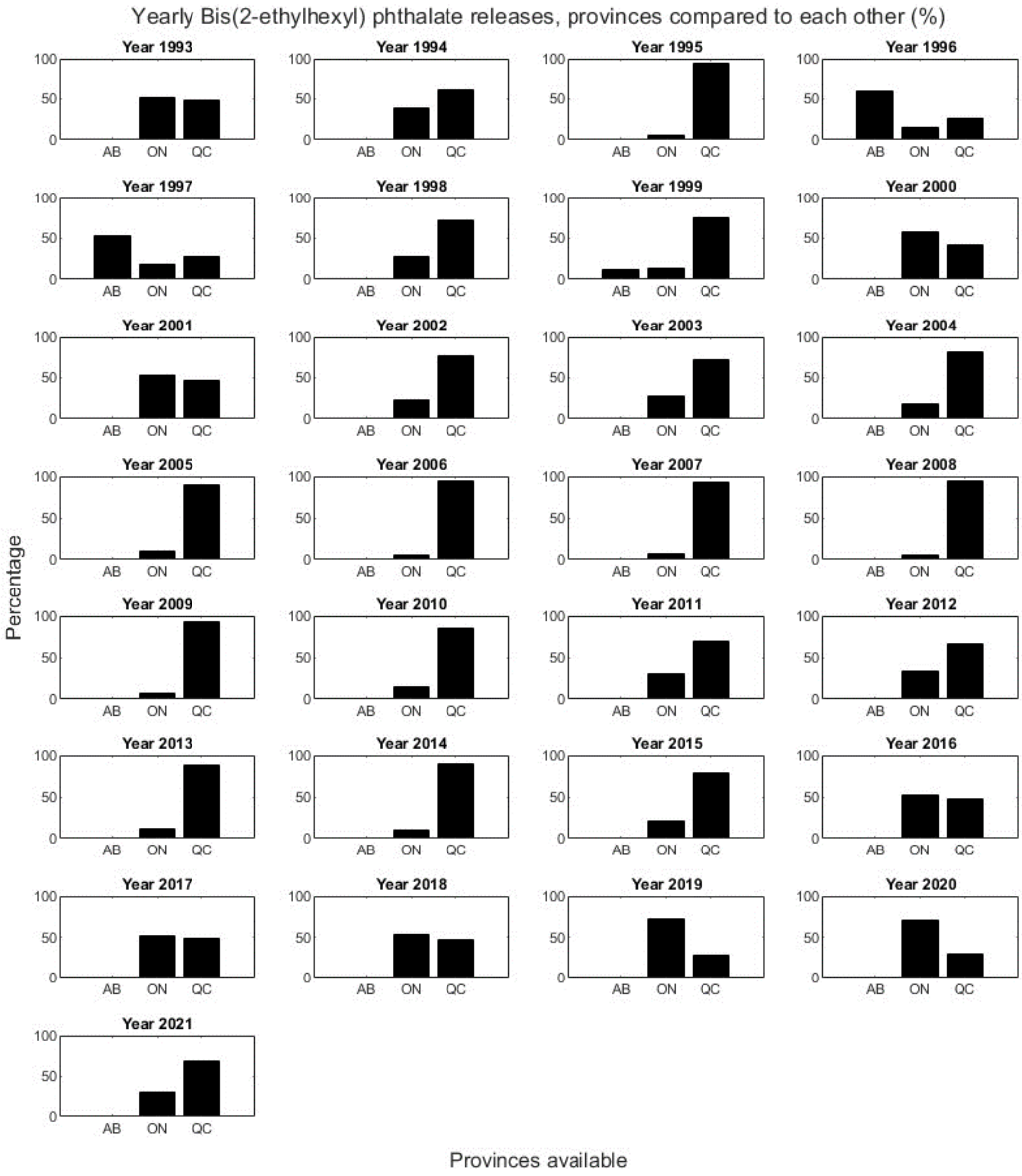

Figure 31- Percentage of Phthalate released in total in each of the provinces

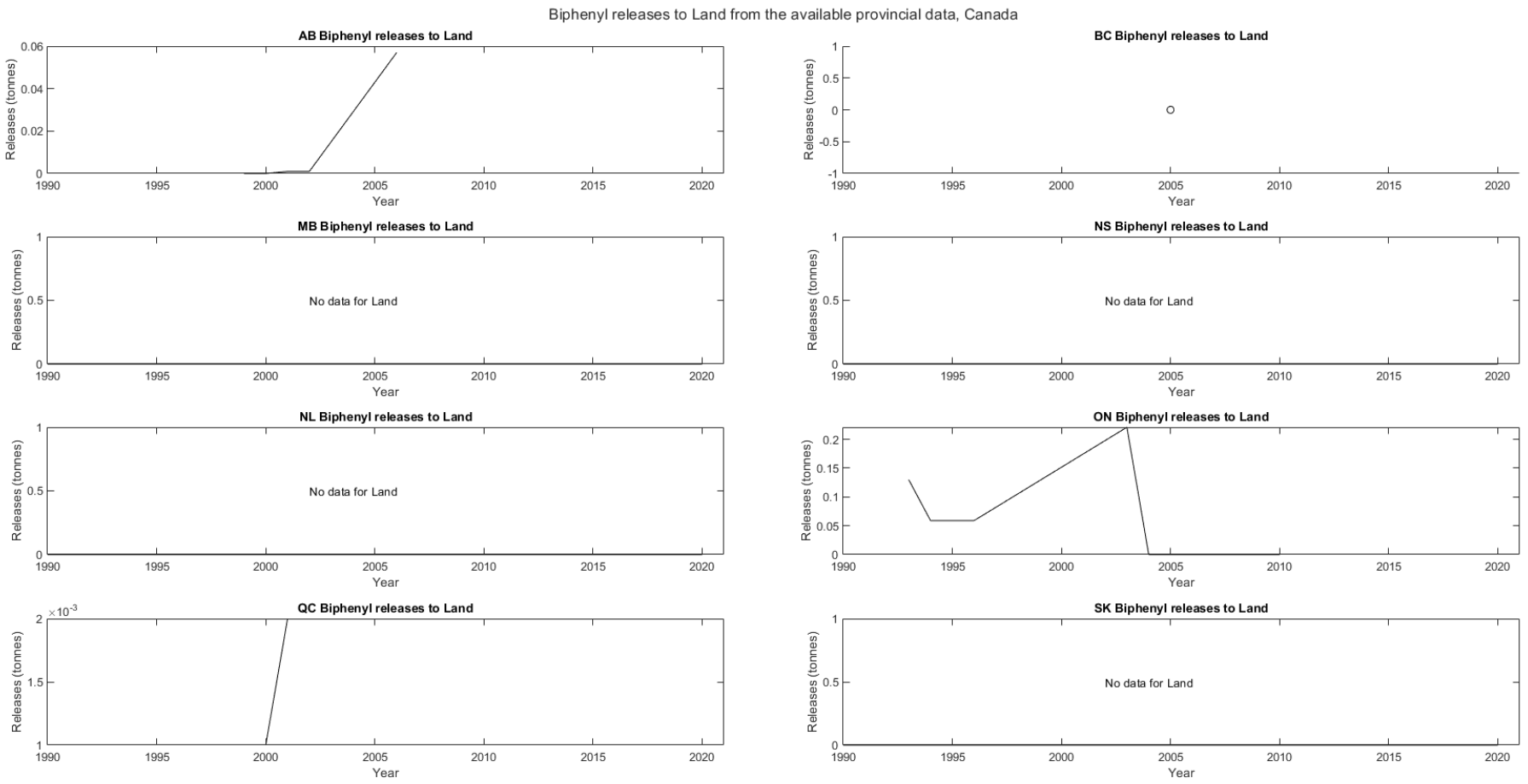

Figure 32-Biphenyl releases compared between the provinces, ejected to Land sites

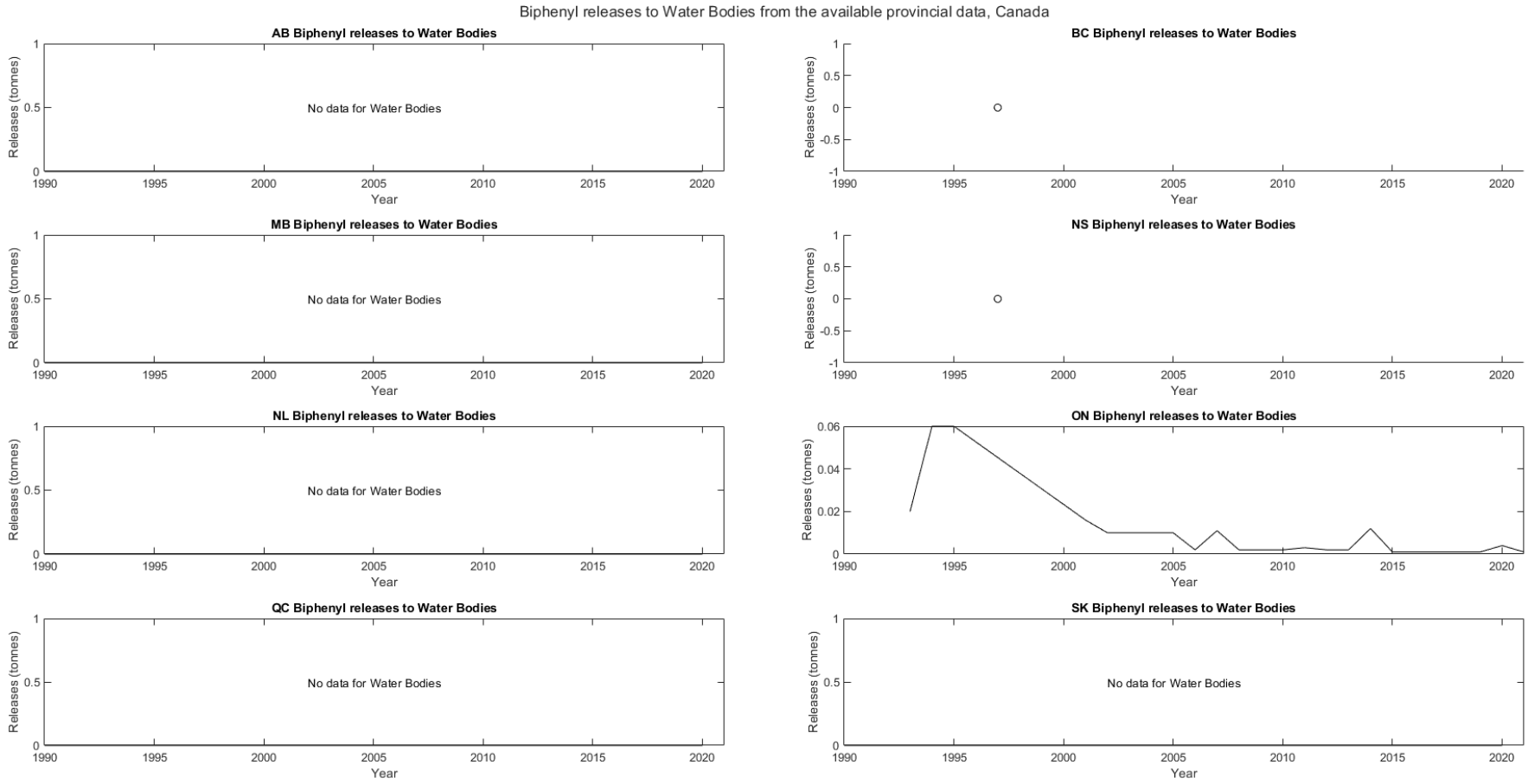

Figure 33-Biphenyl releases compared between the provinces, ejected to Water Bodies

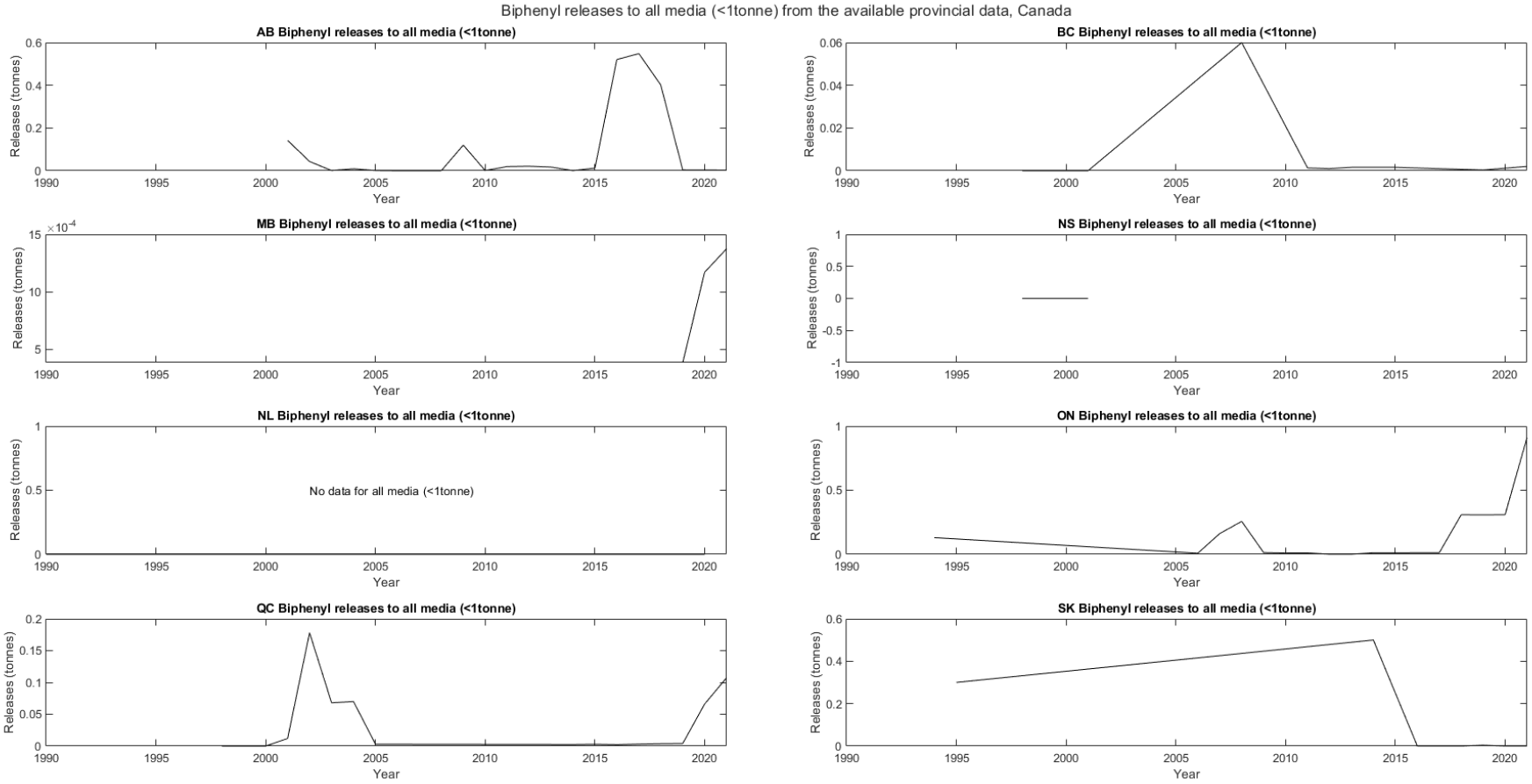

Figure 34-Biphenyl releases compared between the provinces, getting ejected to all media (<1 separately)

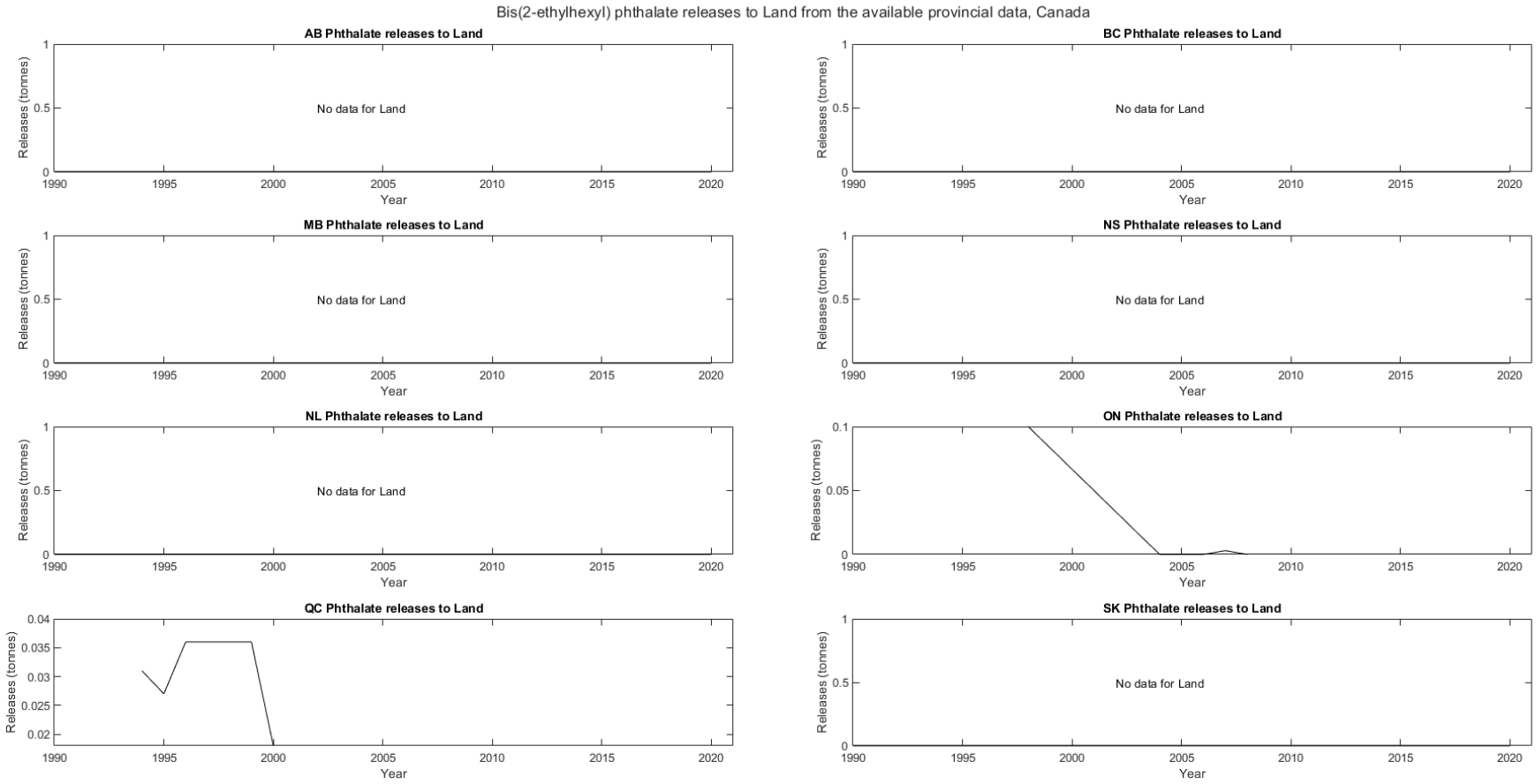

Figure 35-Bis(2-ethylhexyl) phthalate releases compared between the provinces, getting ejected to Land

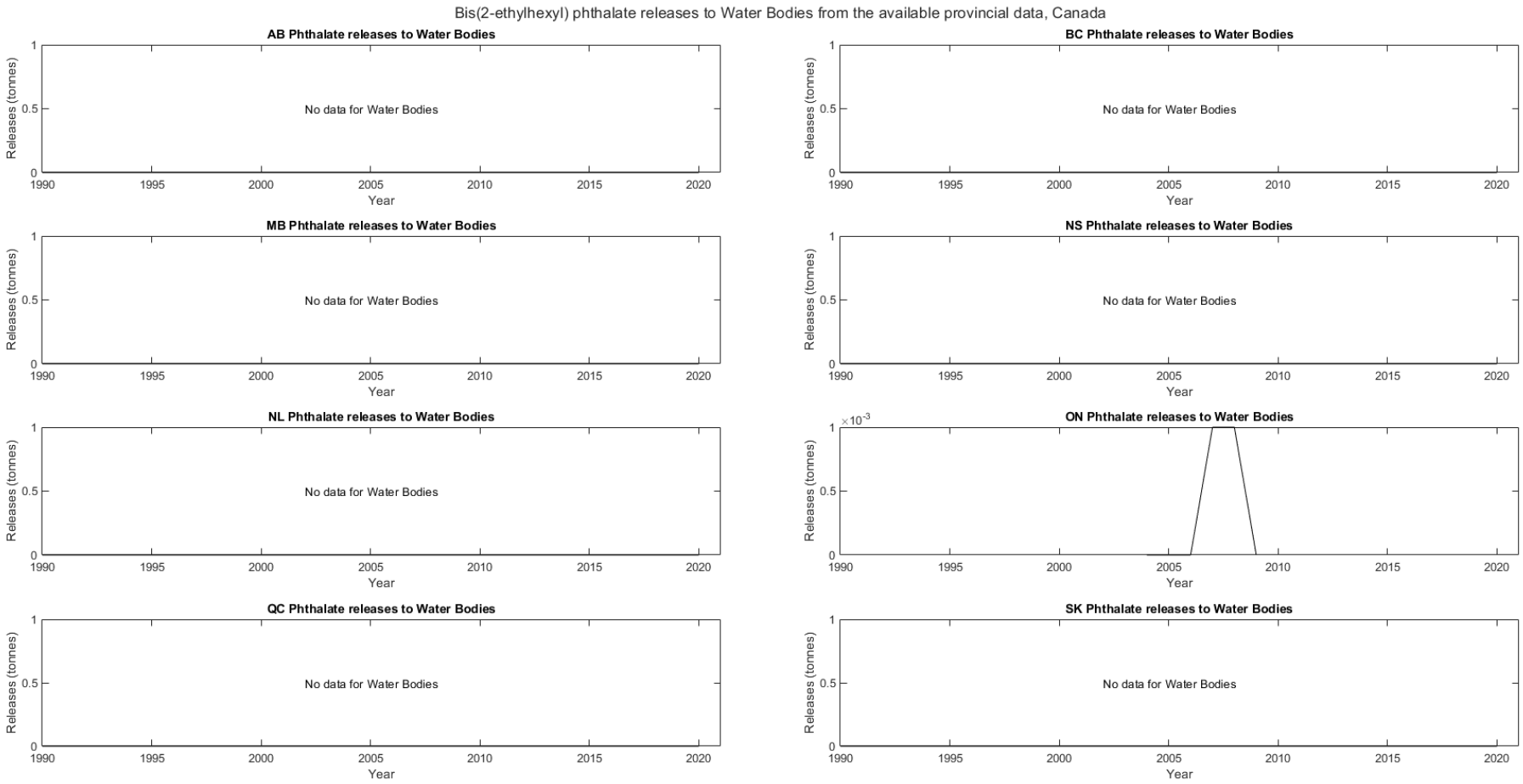

Figure 36-Bis(2-ethylhexyl) phthalate releases compared between the provinces, getting ejected to water bodies

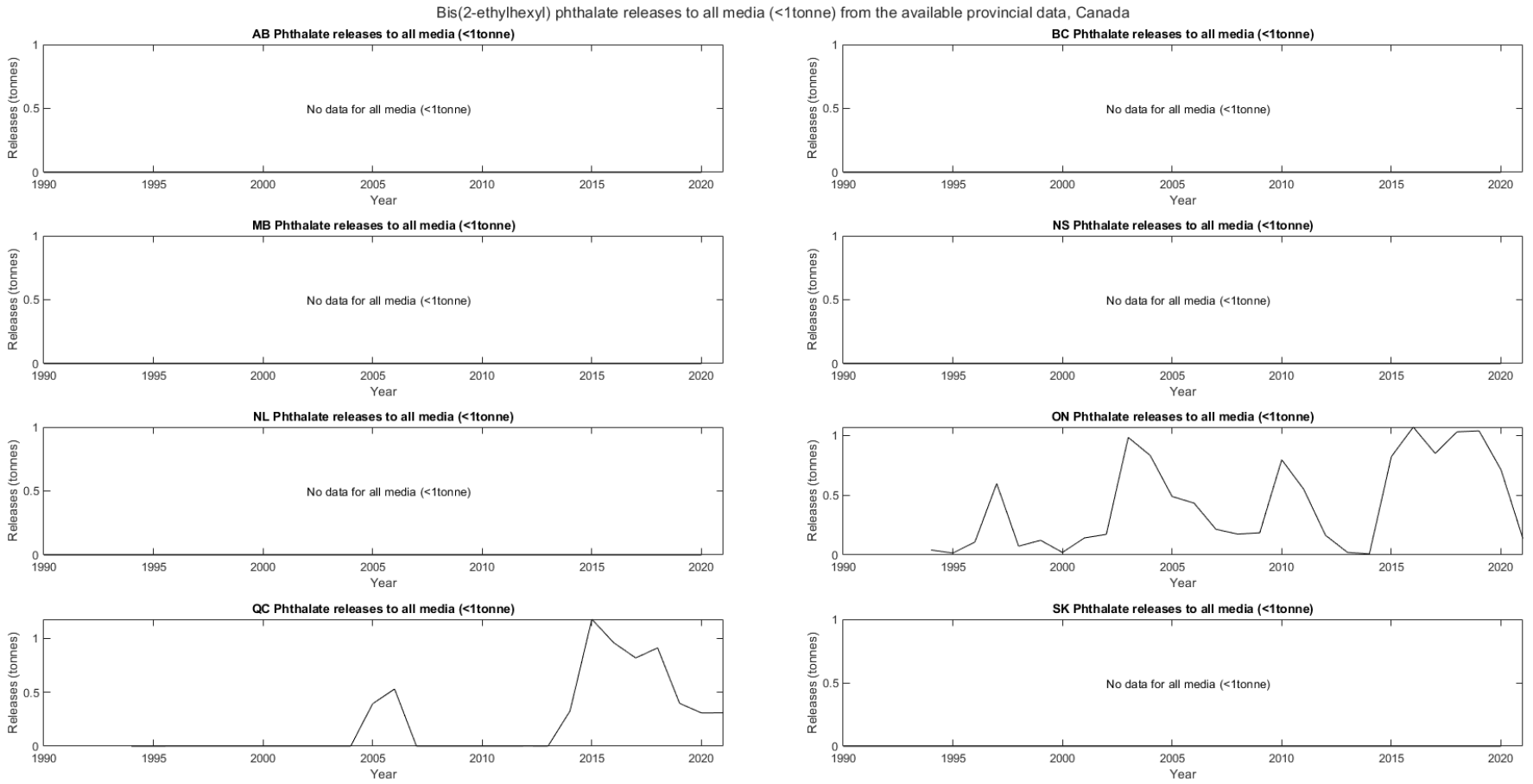

Figure 37-Bis(2-ethylhexyl) phthalate releases compared between the provinces, getting ejected to all media (<1 separately)