ECOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

MASTER THESIS

Pollution assessment of the landfill of Mbeubeuss and the natural urban reserve of the Grande Niaye of Pikine in Dakar, Senegal

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Abstract

This project aims to assess the degree of pollution of an "ecological bomb", sadly known in West Africa, the landfill of Mbeubeuss. Each year, 1 million tons of garbage continue to be accumulated on this open-air discharge, now covering a surface of 114 hectares, i.e. about 160 soccer field (Ministère de l'urbanisme, du logement et de l'hygiène publique et al., 2019).
To this end, analysis in heavy metals, PAHs and PCBs are conducted with state-of-the-art instruments on environmental samples of soil, sediment, superficial water and groundwater from the landfill. The results are compared with the contamination level of a hypothetically better preserved wetland zone: the urban nature reserve of the Grande Niaye of Pikine. Moreover, the study focuses on several tire related pollutants (benzothiazole derivatives, DPG, CHA, AN, 6PPD and its subproduct 6PPDQ), which have been gaining interest in the past years due to their high toxicity (Baensch-Baltruschat et al., 2020).

This work demonstrates the high level of pollution of both sites, by highlighting the exceeding of several environmental norms and quality standards. It provides new information on PAHs, PCBs and tire related compounds concentrations and confirms previous published data on heavy metal contamination.

Results show that water chemical quality of both sites do not meet the Environmental Quality Standards defined by the European Union and the guidelines values in drinking water of the World Health Organization (EU, 2013; WHO, 2017). The Thiaroye table, located below the landfill and supplying drinking water for two third of the surrounding population, should not be consumed due to contamination in nitrates, lead and cadmium.
Regarding sediment quality, less than 30 % of the sediments have metal concentration above levels that are likely to be associated with adverse biological effects for aquatic organisms. Only one soil sample from the landfill area shows a metal content exceeding guide values of the Swiss legislation, compromising its long term fertility (Osol, 1998). The values of POPs concentration in sediments measured in Dakar during this investigation are also lower than the guidelines values, suggesting no toxic effect on sediment-dwelling organisms (Macdonald et al., 2000; Smith et al., 1996).
At least one tire additive is detected in 80 % of the water samples and in 70 % of the soil and sediment samples. The high number and/or concentration of tire related compounds detected in soils close to tire dumping sites in Mbeubeuss suggests that they can be a source of emissions of tire compounds in the environment, in addition to road traffic. All additives are below the toxic levels of various aquatic organisms in water samples ($LCOE$ and EC_{50} from Liao et al., 2018; Tian et al., 2022).

Keywords: heavy metals, persistent organic pollutants, tire-related compounds, wetland, Mbeubeuss landfill, urban reserve, pollution assessment, municipal solid waste

Résumé

Ce projet a pour objet l'évaluation du degré de pollution d'une "bombe écologique", tristement connue en Afrique de l'Ouest, la décharge de Mbeubeuss. Chaque année, 1 million de tonnes d'ordures continuent de s'accumuler sur cette décharge à ciel ouvert, qui couvre désormais une surface de 114 hectares, soit environ 160 terrains de football (Ministère de l'urbanisme, du logement et de l'hygiène publique et al., 2019).
À cette fin, des analyses en métaux lourds, HAPs et PCBs sont réalisées avec des instruments de pointe sur des échantillons environnementaux de sols, de sédiments, d'eaux superficielles et d'eaux souterraines provenant de la décharge. Les résultats sont comparés avec le niveau de contamination d'une zone humide dont on fait l'hypothèse d'une meilleure préservation : la réserve naturelle urbaine de la Grande Niaye de Pikine. De plus, l'étude se penche sur plusieurs polluants liés aux pneumatiques (dérivés de benzothiazole, DPG, CHA, AN, 6PPD et son sous-produit 6PPDQ), qui ont suscité un intérêt croissant ces dernières années en raison de leur forte toxicité (Baensch-Baltruschat et al., 2020).

Ces travaux démontrent le haut niveau de pollution des deux sites, en mettant en évidence le dépassement de plusieurs normes environmmentales et standards de qualité. Ils apportent de nouvelles informations sur les concentrations en HAPs, PCBs et composés liés aux pneus et confirment les données publiées précédemment sur la contamination en métaux lourds.
Les résultats montrent que la qualité chimique de l'eau des deux sites ne répond pas aux normes de qualité environnementale définies par l'Union Européenne et aux valeurs recommandées par l'Organisation mondiale de la santé pour l'eau potable (EU, 2013; WHO, 2017). La nappe de Thiaroye, située en contrebas de la décharge et alimentant en eau potable les deux tiers de la population environnante, ne devrait pas être consommée en raison de sa teneur en nitrates, plomb et cadmium.
En ce qui concerne la qualité des sédiments, moins de 30% des sédiments présentent une concentration en métaux supérieure aux niveaux susceptibles d'être associés à des effets biologiques néfastes pour les organismes aquatiques. Un seul échantillon de sol provenant de la décharge présente une teneur en métaux supérieure aux valeurs recommandées par la législation suisse, indiquand une fertilité à long terme compromise (Osol, 1998). Les valeurs de concentration de POPs dans les sédiments mesurées au cours de cette enquête sont également inférieures aux valeurs recommandées, ce qui suggère qu'il n'y a pas de risque de contamination par les POPs pour les organismes benthiques (Macdonald et al., 2000).
Au moins un additif des pneus est détecté dans 80% des échantillons d'eau et dans 70% des échantillons de sol et de sédiments. Le nombre élevé et/ ou la concentration des composés liés aux pneus détectés dans les sols à proximité des sites de décharge de pneus à Mbeubeuss suggère que leur dépôt peut être une source d'émissions de dans l'environnement, en plus du trafic routier. Tous les additifs sont inférieurs aux niveaux de toxicité de divers organismes aquatiques dans les échantillons d'eau (Liao et al., 2018; Tian et al., 2022; AGI; UE).

Mots-clés: métaux lourds, polluant organique persistant, composés liés aux pneus, zone humide, décharge de Mbeubeuss, réserve urbaine, évaluation de la pollution, déchets solides municipaux

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Glossary

BMW Biomedical waste. 1, 4

EQS Environmental quality standards. 24, 32–34

EU European Union. i, ii, 24, 32, 41, 53, 58, 67

GVDW Guideline value in drinking water (WHO, 2017). 32–34, 53

HMW High molecular weight PAHs. vii, 40

INERIS National Institute for the Industrial Environment and Risks. 24, 32, 53, 59, 67

LMW Low molecular weight PAHs. vii, 40

LOQ Limit of quantification. 40, 41, 83

MAC-EQS Environmental quality standards expressed as maximum allowable concentration. 24, 32, 67

MSW Municipal solid waste. 1

NTS Non-target screening. 19

PAH Polycyclic aromatic hydrocarbons. i, iii, v, vii–ix, 10, 16, 23, 24, 38–41, 50, 54, 77, 78

PCB Polychlorinated biphenyls. iii, v, viii, 10, 16, 23, 24, 38–42, 50, 54, 77, 78

POPs Persistent organic pollutants. i, 39–41, 54

RT Retention time. 20

std standard deviation. 38, 43, 46

SWM Solid waste management. 1

TRWP Tire road wear particles. 45, 47, 55

UCG Unité de gestion des déchets solides. 3

VGE Environmental Guide Value. 32–34

WHO World Health Organization. i, ii, ix, 24, 26, 32, 33, 53, 63, 67

WWTP Waste water treatment plant. 7

1 Introduction

1.1 Context

The rapid urbanization and population growth of Senegal has posed significant challenges and constraints in the sustainable development of the country. Senegal's urbanization rate increased from 25% in 1960 to 39% in 1988 and 45 % in 2020 (Agence Nationale de la statistique et de la démographie, 2020). The Dakar region alone accounts for 23% of the country's total population in 2020, slightly less than a quarter of the population, and gathers 80% of industrial activities (Pesticide Action Network, 2018).

Facilities and infrastructures (hospitals, schools, industrial and commercial zones, security, etc.) are often deficient in fast growing urban centres. One key service to allow good sanitary conditions for the population is solid waste management SWM. However, the most common waste disposal practices in Africa are landfills (mostly uncontrolled) and indiscriminate dumping, which are associated with different level of environmental and health risks (O. Cissé, 2018). According to data collected in 11 African countries, these techniques represent respectively 38 % and 60 %, much more widespread than other practices such as incineration, recycling, composting or methanization (<3 %) (I. Dladla et al., 2016). The region of Dakar does not escape this rule and throws away all its municipal solid waste (MSW) in the unimproved landfill of Mbeubeuss since 1968.

1.1.1 Sites description

Landfill of Mbeubeuss

Initially, the ground level of the site - located on the slopes of the great wet depression of the Niayes - was raised for the construction of the road of Malika in the 1968's, by bringing in compost from the Bel Air plant. Following the closure of the Hann landfill and the lack of treatment solution for the increasing amount of waste, it was gradually transformed into the discharge of the entire Dakar region.

Today, not only household waste but also industrial waste and biomedical waste BMW containing persistent and hazardous substances end up in the landfill. Indeed, recent studies about BMW management in Dakar showed that a high number of health-care facilities and hospitals were sorting waste inappropriately, mixing hazardous and non-hazardous materials, leading to the elimination of the latter in the regular chain of SWM instead of a proper disposal of hazardous waste (Dieng et al., 2020).

The total amount of waste is estimated to be about 10 million of tons and, each year, 1 million tons of garbage continues to be accumulated on the open-air discharge, now covering a surface of 114 hectares, i.e. about 160 soccer field (Ministère de l'urbanisme, du logement et de l'hygiène publique et al., 2019). Its important extension caused the disappearance of a fraction of the lake of Mbeubeuss, which lies in the north and north-east, reducing its surface area by 13%, as well as the loss of natural areas and farmland providing important ecosystem services, i.e. basins or depressions (called *Niayes* in wolof) coastal dunes and market garden crops.

The exploitation of the place was neither implemented nor long-term planned in a way that protects the local population and the environment, which is why it is classified as uncontrolled landfill, as opposed to a sanitary landfill. The site is not properly layered and there is no leachate recovery system, meaning that all

wastes' leachates containing among other bacteria and virus, directly leak into the soil and reach the groundwater. Moreover, the dump is often the place of spontaneous or deliberate lighting of fire, releasing toxic heavy metals, greenhouse gases and persistent organic pollutants like dioxins, furans, PCBs and PAHs. Pollutants emanating from the discharge reach the surrounding environment and inhabitants of the neighbouring areas through multiple pathways such as air transfer and runoff, but also indirectly due to their use of unsafe water (from aquifers and superficial water) and consumption of contaminated food like eggs, market garden products, livestock and fishery products (Pesticide Action Network, 2005; Wilson et al., 2006).
The aquifer situated under the site of the landfill, called *nappe des sables quaternaires* or *Thiaroye table*, is fed by rainfall infiltration and thus varies annually depending on the rainfall intensity and its exploitation, reaching its higher level after the wet season in November (Ministère de l'environnement et de la protection de la nature, 2011). Complex variations of the table's piezometry were observed but, in a simplified way, groundwater can be considered as flowing from the south east to the north east of the discharge and its depth is varying from shallow (0.5 to 5 m deep) to outcropping (Niang et al., 2012). The groundwater is consumed by about two third of the neighbouring population even if its chemical and bacteriological quality is under the norms recommended by the World Health Organisation for drinking water (O. Cissé, 2018; Ministère de l'urbanisme, du logement et de l'hygiène publique et al., 2019; Niang et al., 2012; Wilson et al., 2006). The consumption of water containing pathogenic organisms can cause several waterborne disease like shigellose, salmonelose or hepatite A. Moreover, the environmental exposure to lead and cadmium of the neighbouring inhabitants may provoke chronic adverse health effects such as kidney injuries (Mathilde Cabral et al., 2021). On the city-wide scale, more than 70% of the water supply comes from the groundwater table, the rest being provided by water from the lake of Guiers (Ndiaye, 2009)

A closure and rehabilitation project launched by the State of Senegal, the "Communauté des Agglomérations de Dakar" (CADAK) and the "Communauté des Agglomérations de Rufisque" (CAR) is underway to make the landfill safe (République du Sénégal, decree n° 2010-791 of June 21, 2010). To ensure the safety of the site, it should include, among other works, containment dikes, leachate collection system, final coverage of the site, control and regulation of the water table around the site (Ministère de l'urbanisme, du logement et de l'hygiène publique et al., 2019).
Moreover, a technical landfill center of international standard will be built for waste disposal in a new municipality. Diass and Sindia sites were proposed but the populations of these communities were strongly opposed to the project, considered by the latter as a second Mbeubeuss, presenting high sanitary risks O. Cissé, 2018. Despite numerous studies, the project of closure and rehabilitation of the site and the construction of a new waste treatment facility is still on hold.

The following categories of waste entered the landfill in 2020 (Figure 1 gives their distribution):

- *Complex household waste:* it designates complex packaging, composed of several different materials that cannot be separated (paper, plastic, aluminum).

- *Unclassified combustibles:* they are mainly leather, bones, condoms, rubber and tires.
- *Unclassified non-combustible materials:* they include packaging, rubble, stones, shells, ceramics, tiles, porcelain and flower pots.
- *Special household waste:* ink bottles, nail polish, soiled packaging (paint, nail polish remover, methylated spirits), syringes, bottles of mosquito repellent and medicines.
- *Fine waste*: this category has a diameter of less than 20 mm and is composed mainly of sand and ash.
- *Textile waste:* they are made of fruit or vegetable fillets, clothes, rags, socks, pantyhose, cloth bags, wools, diapers, sanitary napkins, handkerchiefs and other wicks.
- *Putrescible waste:* waste capable of being decompose rapidly such as food scraps, vegetables, turf, etc.
- *Paper and cardboard waste:* linked to industrial, administrative and commercial structures.
- *Wood waste:* derived from areas with commercial activities and carpentry workshops.
- *Plastic waste:* widely used as packaging in the retail, restaurant, real estate and clothing industries.
- *Glass:* wastes coming mainly from administrative, commercial and industrial areas due to high reuse rate of glass in households.
- *Metals:* they come from small and medium-sized enterprises (SMEs) such as metal carpenters, car garages, plumbers.

Large quantities of tires, counted as unclassified combustibles on Figure 1, were stored on the discharge and likely contributed to the degradation of the environment. They represented health and safety hazards due to their use to start fires (at the Mbeubeuss landfill for wate sorting and in other parts of the city during demonstrations), which released toxic fumes. That is why, since 2003, a partnership between the "Unité de gestion des déchets solides" (UCG) and Sococim, a cimentery factory, has been created, allowing the removal of more than 250 tons of end of life tires from the arteries of Dakar and thus avoiding their disposal in the landfill. Moreover, in 2020, they organised a collection campaign to remove directly some of the tires located at the discharge level (Ndour, 2021; Unité de coordination de la gestion des déchets solides, 2020).

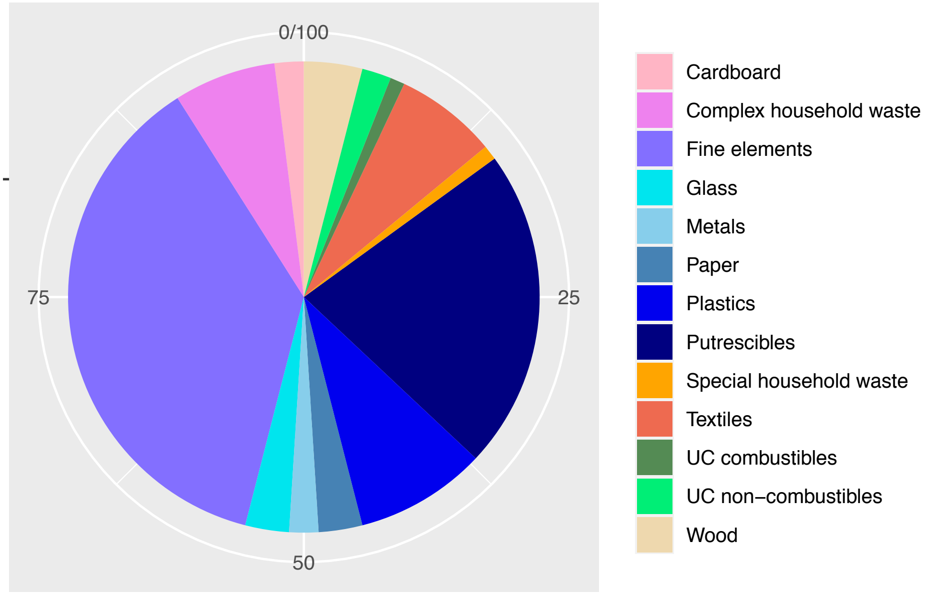


Figure 1: Distribution of waste entering the landfill by category in 2020 (PAGE, 2021).

Potential sources of organic contaminants are present in a greater proportion in industrial waste and BMW and include electrical waste (cable, batteries and accumulators, ink cartridges), chemical and pharmaceutical products (manufacturing scraps, expired products, tablet powder, radioactive waste,...), liquid waste (petroleum products, paint, varnish, dye, used solvent, expired liquid products, oils and fats), anatomical wastes and infectious materials.

An association of recuperators named *Bock Diom* was created in order to recycle the waste of the dump. About 1'650 people of different ages, 26% of whom are women, are working as recuperator and collect in total about 60 kg of waste each day (WIEGO, 2020). The most coveted materials by the recyclers are (by order of preference):

1. Light and heavy iron,
2. Light and heavy aluminium,
3. Heavy and light plastic,
4. Copper,
5. Bronze (copper and tin alloys),
6. Waste Electrical and Electronic Equipment (WEEE),
7. Organic waste,
8. Potting soil,
9. Paper and cardboard.

The recovered materials are then valorised by the informal sector but also by the formal industry. Recovery channels for the material of interest in this study are given in the following table:

Table 1: Landfill waste recovery chain from O. Cissé, 2018

Waste	Valorisation	Actor
Scrap metal	Foundry and recycling of concrete iron, recycling in post for construction, artisanal manufacture of stoves, basins, watering cans, funnels	Local foundrymen
	Industrial recycling (48'000 tons) and export	SOMETA
Non ferrous metals	Artisanal manufacture of pots (aluminum), industrial manufacture of batteries (lead), manufacture of bracelets, rings (bronze), export for recycling (copper, aluminum, brass)	Local foundrymen
	Industrial aluminium recycling (5-8 tons)	SELMEG
Rubber	Manufacture of sinks, tensioners for bicycle and link, with inner tubes, cutting of harnesses in tires	Recuperators/ craftsmen

Urban Nature Reserve of the Great Niaye of Pikine

The Great Niaye of Pikine, commonly called Technopole, has been established as an Urban Nature Reserve by the decree n° 2019-748 of March 29, 2019 due to its high ecological value. Similar to the areas surrounding the landfill, this site is also characterized by a depression (a so-called *Niaye* in wolof), where water from the water table and rainwater converge. *Niayes* are wetland typical from the Great Senegalese Coast, which comprise the largest cities of the Country (Dakar, Thiès, Louga, Saint-Louis), and begin to form during the Quaternary period. At that time, the landscape was made of successive spits, lagoons and interdunal lakes. Spits are linear strips of accumulation of sediments off coast, which are initially hooked at both ends, separating low areas from the sea. They can then take different forms (lagoon, cuspate forelands, barrier island, tomobolo, etc.) but have in common their slight elongated relief and their alluvial nature (Badiane et al., 2018). In response to changes in climate and to sea level variations, the landscape has evolved into a wetland with specific characteristics, transforming it into a unique natural heritage for the city with high agronomic value (K. Diop et al., 2019). Figure 2 shows the localisation of wetlands in the region of Dakar.

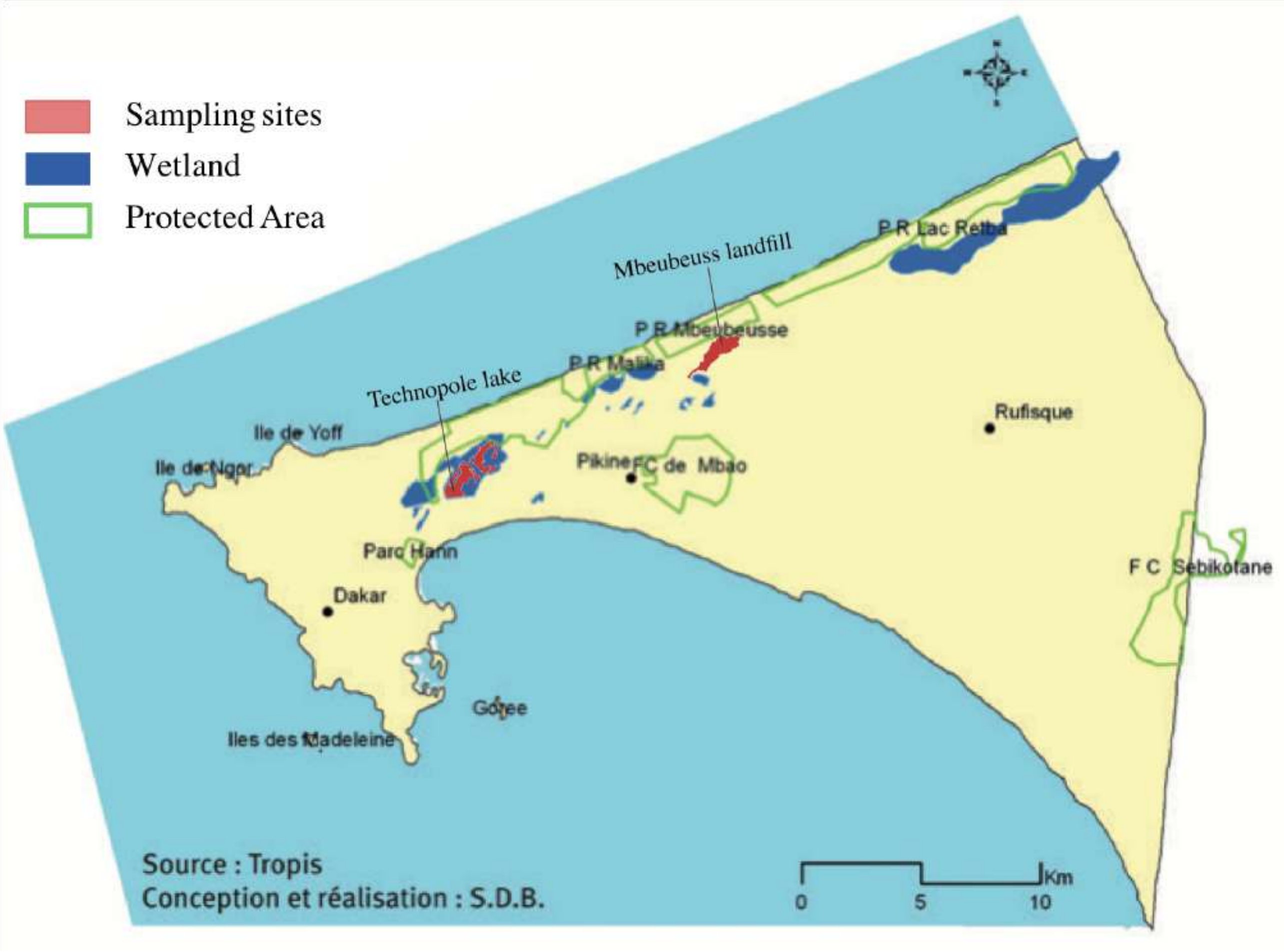


Figure 2: Localisation of wetlands in the region of Dakar, including Mbeubeuss lake and the Grande Niaye of Pikine from Badiane et al., 2018.

Wetlands are urban green lungs, sheltering a rich fauna and flora (mainly avifauna, reptiles, fresh or brackish water fish, aquatic plants and woody plants) and providing important ecosystem services. The Technopole site is, for instance, a place of reproduction and migratory stages for the avifauna, composed of more than 239 species of birds, and a habitat for a diverse flora with over 260 identified species.

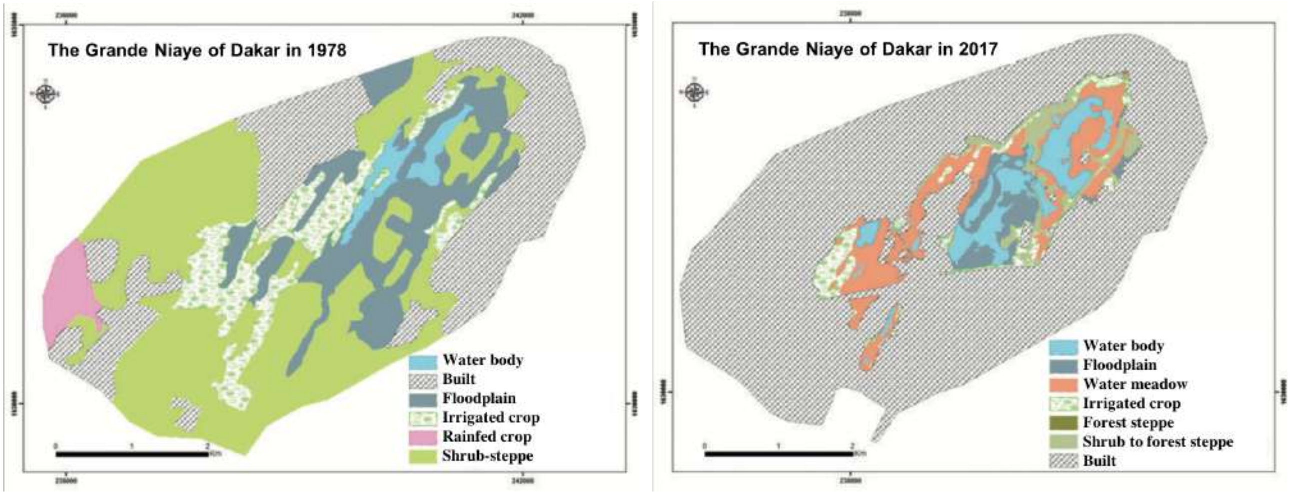
Badiane et al. evaluated the ecosystem goods and services of each *Niaye*. The urban reserve counts twenty one services, of which five of supply, five of regulation, eight cultural services and three of biodiversity support, while Mbeubeuss provides ten services distributed as follow: three of supply, two of regulation, three of biodiversity support and two of cultural services.

In addition to that, the horticultural production of the country is carried out to 80% in the *Niayes*, which makes it an important economic region for the country. The average annual production in the Dakar region, second horticultural region after Thiès, accounted for 25% of the national production between 1995 and 2000. The market value of wetland services in terms of annual mean income for horticulturists was estimated to respectively 7 634 euros for Technopole and to 1 221 euros for Mbeubeuss in 2013 (K. Diop et al., 2019).

The conservation of these important areas is a real challenge due to the rapid growth of the city, which results

in an increasing urban pressure. The population of the *Niayes* (including Dakar, Thiès, Louga and Saint-Louis) for the year 2020 is 8'169'191 (about 50% of total population) compared to only 2'550'000 in 1976 (Agence Nationale de la statistique et de la démographie, 2020; K. Diop et al., 2019). The Dakar region alone contains 23% of the country's inhabitants. Senegal's urbanization rate increased from 25% in 1960 to 39% in 1988 and 46 % in 2018.
Moreover, a high number and amount of pesticides, including pesticides prohibited by international regulations, are used in an uncontrolled way in the market gardening zones of the Niayes periurban area. In decreasing order of importance (in terms of number and quantity) the following pesticides are in circulation : organophosphates (54%), carbamates (21%), organochlorines (9%), pyrethroids (6%) and other unidentified products (10%) (République du Sénégal, 2021). A study carried out by A. Diop revealed the presence of 17 phytosanitary products in soils and 15 in vegetables and groundwater (out of 21 analysed) samples from four sites in Dakar, including Malika (very close at the south of the landfill) and two sites located at a few km north and east of the Technopole. Thus, the actual practices employed for horticultural production are partly responsible for the degradation of the *Niayes*.

Figure 3 highlights the loss of the wetland ecosystem due to a rapid progression of urbanization around the Grande Niaye of Pikine. Indeed, in the technopole area, as in other wetland regions, road infrastructure, residence places and public facilities have been built and agricultural land has been converted to residential areas. As en example, seven hectares have been destroyed for the construction of the national arena. The main roads of Senegal are located south of the site: the highroad A (average daily toll transaction of 60'608 in 2015 for Dakar-Diamnadio according to Eiffage), the national road N and the secondary roads D and VU.



(a) 1978 (b) 2017

Figure 3: Evolution of soil use in the Grande Niaye of Pikine from 1978 to 2017 (Badiane et al., 2018).

In the area of Technopole is located one of the three waste water treatment plants (WWTPs) of Dakar: the WWTP of the Niayes, as well as the Golf Club's recreational grounds and the ONAS's (National Office of Sanitation of Senegal) sanitation infrastructure. Different companies have also established their administrative complexes such as ADIE (state IT agency) and SONATEL (Senegalese telephone operator).

Nevertheless, the remaining portion of the Niaye of Technopole seems less marked by a direct anthropic threat compared to the Mbeubeuss site, whose surface continues to decrease due to the disposal of waste. Moreover, its registration as an urban nature reserve in 2019 reflects the state's desire to preserve this site and paves the way for the implementation of appropriate technical and institutional solutions to protect wetland.

1.2 Tire related pollution

Tire microparticles (TP) are a major source of microplastics (MP) present in multiple environmental compartments: soil, surface water, sediment, groundwater, etc. (Halle et al., 2019). It is estimated that they account for 5 to 10 % of the overall amount of plastics ending up in our oceans (Pieter Jan et al., 2017).
TP found in the environment originate mainly from road traffic, as a result of the friction of tires on the road (ibid.). The resulting mixture of road pavement and tire particles is named tire and road wear particles (TRWP) and it is estimated that mineral encrustation from the road reduce its tire content by two (Kreider et al., 2010).
Tire wear emissions can be atmospheric or deposited on the roadsides. It has been estimated that 90 to 99.9 percent of the emissions are non-atmospheric (Panko et al., 2013). Once deposited, tire wear particles are transported by stormwater runoff and can contaminate surface water, groundwater and soils, especially if pavement water is not collected and treated at a wastewater treatment plant (Huber et al., 2016). It has been estimated that 18% of generated tire wear particles reach freshwater (K. Unice et al., 2019).

Production of synthetic and natural rubber has been raising in the past years, increasing from around 17.68 million metric tons in 2000 to approximately 27.4 million metric tons in 2020 (statista, 2021). It has been estimated that annual emissions of TRWP range from 0.2 to 5.5 kg/(cap*a) (Baensch-Baltruschat et al., 2020).

TRWP may lead to toxicological effects related either to the substances they release (i.e. leaching of heavy metals or additives) or to the particle itself, causing physical damage (ibid.). Wagner, Hüffer, et al. compile studies about the effect of tire wear or TWRP from road simulator leachates on aquatic species, in the absence of soils or sediments. Accute effect was observed in a range of 25- 100'000 mg TWP/L and chronic effect concentrations vary from 10 to 3'600 mg TWP/L.
The concentrations at which acute and chronic toxicity on aquatic species have been observed are higher than reported environmental concentrations, which do not exceed 10 mg TWP/L in settling ponds and river water. Nevertheless, most studies do not reflect real environmental conditions due to the use of leachates and no real TRWP. Indeed, Kreider et al. showed that particles from road simulator and cryogenic milled tire particles (CMTP) differ from real TRWP in either morphology, size distribution, or chemical composition.

Tires content

The typical composition by weight of tires is as follows (Sommer et al., 2018; Wagner, Hüffer, et al., 2018):

- Rubber/ Elastomer 40-50%
- Softener (oils and resins) 15%
- Fillers/ Reinforcing agent (soot/ carbon black, clays, silicas, calcium carbonate) 30-35%
- Reinforcing materials (steel, polyester, rayon, nylon) 5-10%
- Vulcanization agents (sulphur, zinc oxide, etc.) 2-5%
- Additives 5-10%

Tires are actually a complex mixture of these different elements. Indeed, typical all-season car tire contains approximately 30 types of synthetic rubber, 8 types of natural rubber, 8 types of carbon black, steel, polyester and nylon fibres, copper and 40 different chemical compounds, resins, oils, pigments, silica and clays. The composition of tires vary between brands and depend on their purpose, i.e. whether it is a winter or summer tire and whether it is a truck, motorbike or car tire. Truck tires are more resistant thanks to a higher natural rubber content (about 80%), whereas passenger cars are mainly made of synthetic rubber, containing only about 15% NR (Wagner, Hüffer, et al., 2018). Natural rubber (NR) is a polymer made of the organic compound isoprene, whereas synthetic rubber (styrene butadiene rubber (SBR) or butadiene rubber (BT)) are derived from the styrene and butadiene monomers.

The high number of additives present in tire include preservatives (halogenated cyanoalkanes), anti-oxidants (amines, phenols), desiccants (calcium oxides), plasticizers (aromatic and aliphatic esters) and processing aids (mineral oils, peptisers)(ibid.) and the main heavy metal of tire tread is zinc with a content of 1% wt.(Councell et al., 2004). The composition of used tires is modified due to their interaction with the road through friction and heat and the incorporation of materials from the road or from the atmosphere such as minerals or brake dust. It is estimated that TRWP released in the environment are made of around 50 % of tire and 50 % of mineral encrustations (Kreider et al., 2010).

Detection of tire wear in the environment

In order to quantify the amount of tyre particles in the environment, it is possible to rely on the concentration of tyre-specific markers. The markers used are either heavy metals such as zinc, sulphide or organic compounds, such as benzothiazoles or 6-PPD (N-(1,3-dimethylbutyl)-N0 -phenyl-1,4- phenylenediamine). However, this approach has limitations as the sources of these markers are sometimes multiple and their quantity may vary from one tyre to another. Indeed, there are differences between tyre types and brands and the concentration of these compounds varies as a result of the interaction of tyres with the external environment. The analytical technique used to separate heavy metals from other elements in the sample is acid digestion extraction and their concentration can then be measured by ASS, ICP-OES or ICP-MS. Another approach is to detect the rubber in the tyres. Given its high molecular weight, it is necessary to use destructive measures, such as pyrolysis, to generate volatile gases that can then be analysed by gas chromatography, either GC-FID or GC-MS. The most common markers generated by pyrolysis of rubber that are determined by GC are dipentene (isoprene dimer) for natural rubber and vinylcyclohexene (butadiene dimer) for SBR (Wagner, Hüffer, et al., 2018).

1.3 Research objectives

Several studies assessed the impact of the landfill on the environment and on the local population through socio-economic studies as well as measurement of heavy metals and bacterial quality of groundwater, soils and animal products like eggs, poultry breeding and pig farming. (O. Cissé, 2018; DIEYE, 2009; Institut africain de gestion urbaine, 2011; Mbodji et al., 2021; Ministère de l'environnement et de la protection de la nature, 2011; Ministère de l'urbanisme, du logement et de l'hygiène publique et al., 2019; Missohou et al., 2011; Niang et al., 2012; Pesticide Action Network, 2005; Wilson et al., 2006).
Moreover, some authors focused on the effect of population's exposure to heavy metals (Cabral et al., 2012; Mathilde Cabral et al., 2021) and a few reports took stock of the pollution in persistent organic pollutants in air, soil, water and chicken eggs (Ministère de l'environnement et de la protection de la nature, 2011; Pesticide Action Network, 2018; UN, 2009).
Nevertheless, pollution data is still scarce and the analytical methods used by the laboratories have often high quantification limits, i.e. above quality criteria for pollutants in water, soil and sediment. A constant monitoring of the degree of contamination and a better knowledge of the hazardous substances of the site are needed in order to propose and implement appropriate solutions for the prevention of environmental and health risks.
Therefore, the goal of this project is to give a pollution overview of the area of the Mbeubeuss landfill and to compare it to a better preserved wetland zone: the urban nature reserve of the Grande Niaye of Pikine. Analysis in heavy metal, PAHs and PCBs will be conducted with state-of-the-art instruments on environmental samples of soil, sediment, superficial water and groundwater. Their concentration will be compared with guidelines values to assess their risk on human health and their toxicity for the environment as well as with values obtained in previous published studies.

The huge number of different anthropogenic chemicals being produced globally, estimated to be 350 000, plus unknown substances and by-products, may also have undesired effect on living organisms and on the environment. The analysis of selected contaminants by target screening methods can omit potential chemical stressors and bias the quality assessment of environmental samples. Therefore, non-target analysis (NTA) will be carried out on soil and sediment samples with the goal of detecting and identifying a large number of chemicals and eventually discovering unknown contaminants as well as comparing general characteristics of both sites. Suspect screening will also be performed to restrict the massive analysis and to set priority on environmental relevant chemicals such as pharmaceutics and pesticides, which are widely used in the peri-urban *Niayes* of Dakar (**gueye_pesticides**; A. Diop, 2013; République du Sénégal, 2021).

In addition to the general contamination assessment of both sites, this project will also focus on the pollution associated with tires, which was actually its initial objective. Tire-related pollution has been gaining interest in the past years and studies have been done to quantify tire-road wear particles (TRWP) in various countries, situated mainly in Europe, in the USA and in Asia (Baensch-Baltruschat et al., 2020). A recent study discovered that a chemical derived from a tire additive (6-PPDQ) was responsible for the mass deaths of coho salmon in the Pacific Northwest of the US (Kyoshiro et al., 2021). In Senegal and more broadly in Africa there is to our knowledge no data about TRWP distribution. It is necessary to quantify the accumulation and distribution of tire and road wear particles and their related pollutants worldwide, including in Senegal, in order to assess their impact on the environment. Moreover, there is no banning of end of life tires (ELT) from landfill in Senegal as compared with Europe, which could lead to a new source of tire related pollution. Therefore, the objective is to quantify the pollution related to tires in Dakar by focusing on two potential hot spot of pollution: the landfill of Mbeubeuss, where end-of-life tires are stored, and the urban nature reserve of of the Grande Niaye of Pikine and dependence, located close to the highway.

The hypotheses of this work are the following:

- A correlation exists between the concentration of contaminants and the distance to the landfill.
- Superficial water, soil and sediment of the discharge have a higher degree of contamination than those of the control site (Technopole).
- There is a linear trend between the concentration of tires' particles and additives and the distance to the source of contamination (road or landfill).

2 Material and methods

2.1 Study area and sampling

In accordance with the initial goal of the project, the sites were chosen because of their vicinity to potential sources of tire contamination. A socio-economic survey was conducted in order to have a better knowledge of the tire sector in Dakar and to be able to identify hot spots of tire pollution.
The main sites that emerged from this study were the landfill of Mbeubeuss, an open-air discharge of about 114 hectares where large quantities of tires were stored until a few years ago, and the Urban Nature Reserve the Great Niaye of Pikine, commonly called Technopole (Ministère de l'environnement et de la protection de la nature, 2011). The interest of the Technopole lies in its proximity to the highway, the national and secondary road (see figure 5 section 2.1.1). These roads may be the source of tire microparticles pollution resulting from tires' friction on the road.
Moreover, a general pollution assessment and a comparison of the two sites, both being wetlands area subject to various urban pressures, will be conducted.

2.1.1 Sampling sites

Figure 4 and 5 show the landfill and Technopole areas with the sampling points of the project. The collected samples are summarized on Table 2 and some pictures of the sampling campaign are shown in appendix A.

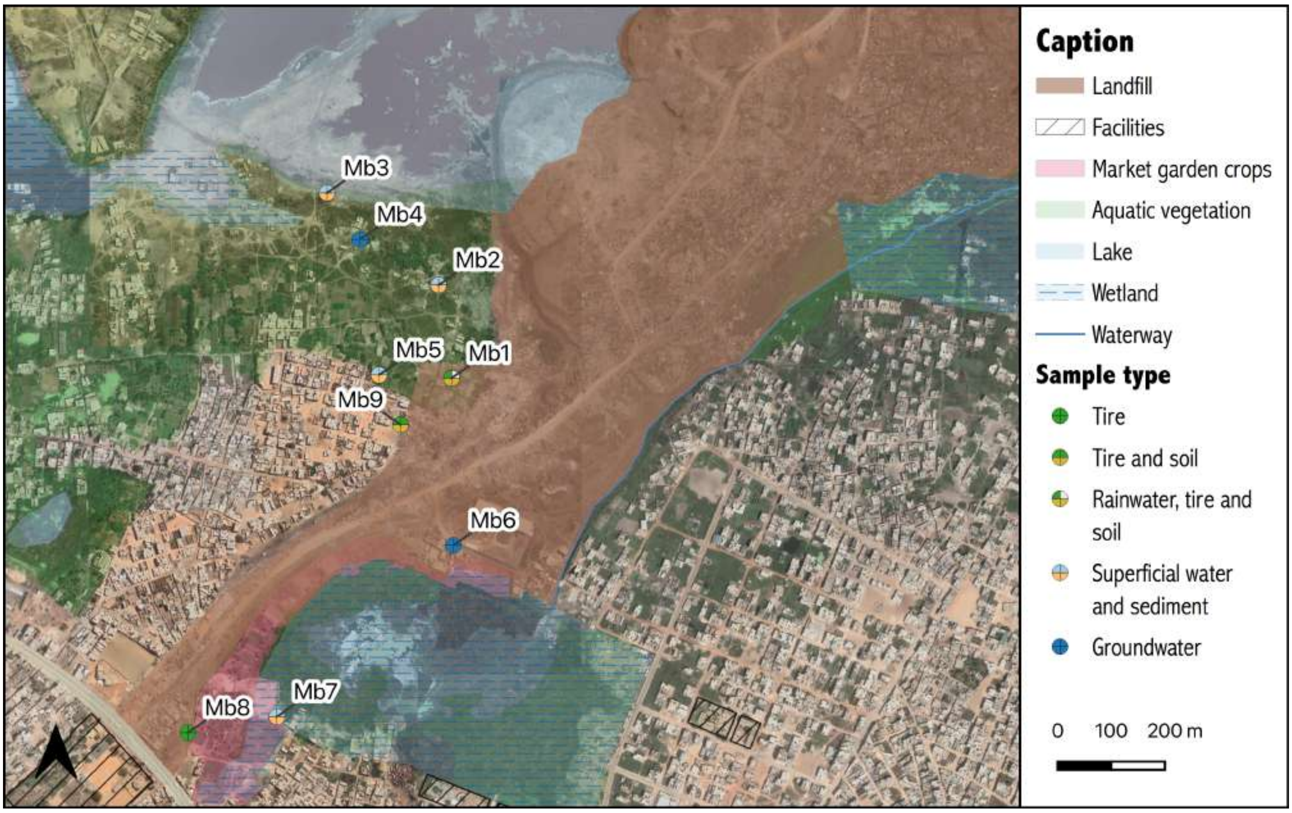


Figure 4: Mbeubeuss landfill

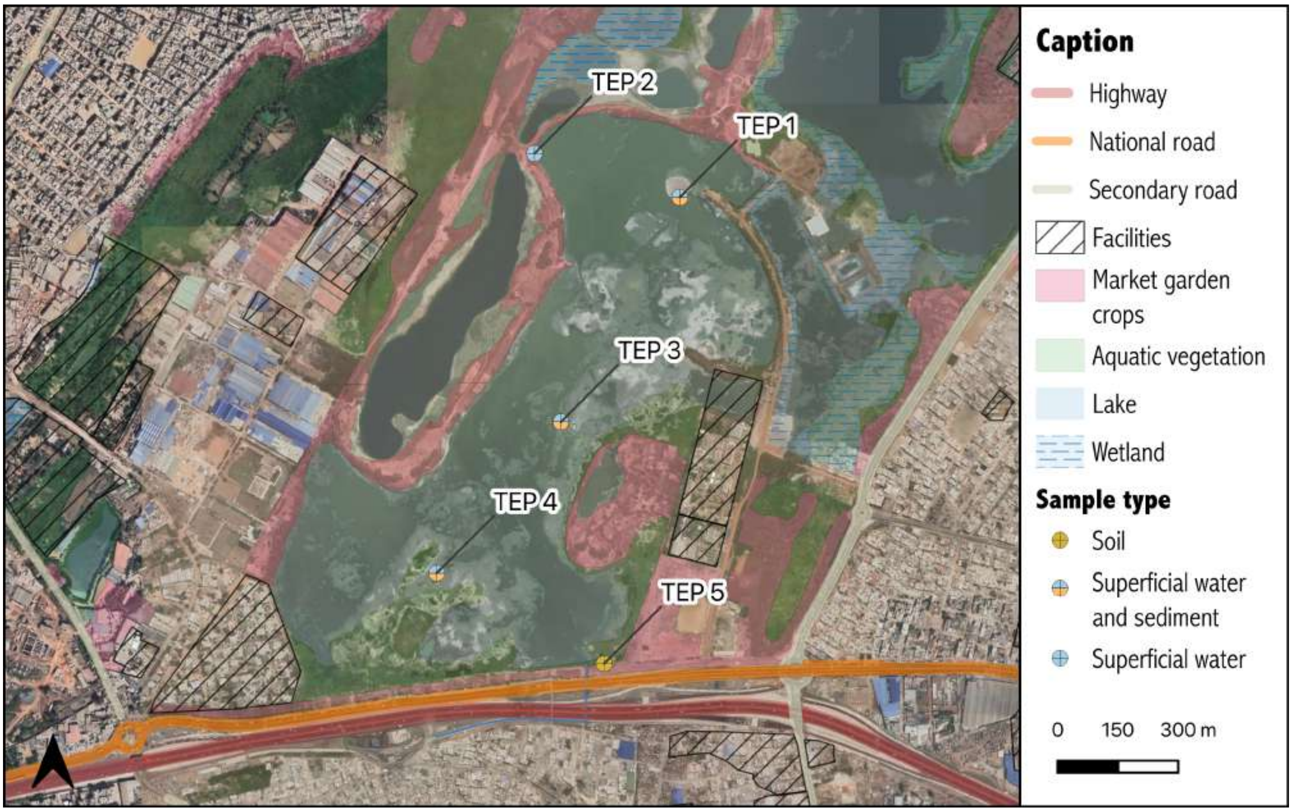


Figure 5: Urban nature reserve of the Technopole

Table 2: Locations and description of sampling sites in Dakar (Senegal)

Sampling site	Sample name	Description	Coordinates	Description of potential pollution sources
Mbeubeuss landfill	MB1s MB1rw	Soil from tire dumping site and rainwater standing in a tire	14°47’49.3"N, 17°19’19.7"W	Household waste, solid industrial waste and biomedical waste from landfill, fertilizer used in horticultural areas, animal manure and discharges from industry
	MB2sed MB2sw	Sediment and surface water from a pond around the landfill	14°47’54.5"N, 17°19’20.7"W	
	MB3sed MB3sw	Sediment and surface water from the lake surrounding the landfill	14°47’59.7"N, 17°19’26.5"W	
	MB4gw	Groundwater from a well close to discharge	14°47’57.3"N, 17°19’25.1"W	
	MB5sed MB5sw	Sediment and surface water from a pond around the landfill	14°47’49.1"N, 17°19’24.0"W	
	MB6gw	Groundwater from a well close to the landfill	14°47’29.2"N, 17°19’30.1"W	
	MB7sed MB7sw	Sediment and surface water from a pond around the landfill	14°47’29.2"N, 17°19’30.1"W	
	MB9s	Soil from tire dumping site	14°47’46.4"N, 17°19’22.7"W	
Technopole lake	TEP1sed TEP1sw	Sediment and superficial water from Technopole lake	14°45’24.8"N, 17°24’44.8"W	Urban water discharge, high traffic roads, fertilizer used in horticultural areas, discharges from wastewater treatment plants (WWTP of Niaye) and discharges from industry
	TEP2sw	Superficial water from Technopole lake	14°45’28.6"N, 17°24’55.6"W	
	TEP3sed TEP3sw	Sediment and superficial water from Technopole lake	14°45’07.5"N, 17°24’53.8"W	
	TEP4sed TEP4sw	Sediment and superficial water from Technopole lake	14°44’55.6"N, 17°25’04.2"W	
	TEP5.1s TEP5.2s	Soil between high traffic roads and Technopole lake	14°44’48.4"N, 17°24’51.0"W	

Sw stands for superfical water, gw for groundwater, rw for rainwater, sed for sediment and s for soil. Coordinates from Technopole sampling sites are approximate as no electronical device could be taken on board the boat.

2.1.2 Environmental samples

The tire pieces were removed from whole tire with a cutter and placed in plastic bags for the transport to Switzerland. The upper layer of the tire treads was cut with a cutting tool into small pieces with a diameter of 5mm before being cryogenically milled (CryoMill Retsch ®) according to the method proposed by Retsch ® for rubber. Tire pieces were placed into two stainless steel grinding jars containing each a grinding ball with a diameter of 25mm. Then, the jars were immersed in liquid nitrogen for 10 minutes and placed in the grinder under the following conditions: 2 minutes at a frequency of 25 Hz. Controls were realised by repeating the same steps with polystyrene (PS) to evaluate possible contamination from the grinding step.

Sediment and soil were collected at varying distances from the Mbeubeuss landfill (0 to 400 meters) and from the highway (5 to 1200 meters) by subsampling the content of a shovel with a spatula. The sediments were placed in plastic bags and the soil in aluminum foil. They were air-dried in the laboratory for two weeks before being transported to Switzerland, then dried again in the oven at 60°C for 2 days, sieved through a 500-µm mesh size sieve and homogenized using pestle and mortar. They were placed into a desiccator until analysis.

For each site, water samples were collected into two 100-mL glass vials. Upon return to the laboratory, filtration at 0.45 μm was performed and nitric acid (HNO_3) was added to the first vial for metal analysis. They were transported from Senegal to Switzerland in a cooler and were then stored at 4°C until performing analysis. Some bottles (MB1/ MB3/ MB6/ MB7/ TEP1/ TEP2/ TEP3/ TEP4) were broken and partially or completely emptied during transportation. Therefore, no analysis of tire additives by SPE and LC-MS/MS could be done on sample MB1 and TEP4, and metals analysis by ICP-MS/MS and ICP-OES was conducted on the bottle TEP1 that had not been dosed with HNO_3.

2.2 Metal analysis in environmental samples

2.2.1 Acid digestion of tire, soil and sediment samples

Tire powder and soil and sediment samples were then acid digested. Triplicates of 250 mg of each tire sample were placed into Teflon vessels. 9 mL of 69% HNO3 and 1 mL of Milli-Q water were added. The vessels were placed into a microwave reactor (multiwave Pro Anton Paar) and heated at 200 °C with the following conditions: 15 minutes heating up to 200 °C, 45 minutes steady conditions at 200 °C and 20 bar, and 10 minutes cooling to 70 °C. Triplicates of 1000 mg of each soil and sediment sample, 3 ml 69 % HNO_3, 6 ml 38% HCl and 1 ml milliQ® water were placed in Teflon vessels. The vessels were heated at 200 °C in the multiwave reactor according to the following conditions: 15 minutes heating up to 200°C, 30 minutes steady conditions at 200°C and 20 bars, and cooling down to 70°C. For each material, the digesta was filtered through 0.45 µm PTFE filters (Chromafil®), placed in volumetric flasks and filled up to 50 mL with milliQ® water. They were then transferred to test tubes and stored at 4°C until analysis.

2.2.2 ICP-MS/MS and ICP-OES analysis

Metal analysis were performed on an inductively coupled plasma (ICP) optical emission spectrometer (Shimadzu® ICPE-9000) and on a triple quadrupole ICP tandem mass spectrometer (Agilent Technologies ICP-MS Triple Quad 8900) for metals present respectively in high and low concentrations. For both instruments, calibration curves were established with 5 to 10 points of appropriate concentration from a multi-element standard solution (Inorganic Ventures). Quality control solutions were processed between a series of 10 samples. When necessary, water samples and microwave digested extracts were 10x, 100x and 1000x diluted. More details can be found in Appendix C.

2.3 PCBs and PAHs analysis in soil and sediment samples

2.3.1 Extraction by ASE

PCBs and PAHs were extracted from dry soil and sediment samples by accelerated solvent extraction (ASE). Glass fiber flters were introduced at the bottom of pre-cleaned 22 ml ASE cells (20 minutes in ethanol and ultrasonic bath). 500 mg of each soil were mixed with hydromatrix and added in ASE cell previously filled sequentially with 5% deactivated neutral alumina (1 g), silica gel 60 (7.3 g), 5% deactivated neutral alumina (1 g). The ASE cells were filled with hydromatrix until 0.5cm of the top, spiked with 50 μL of internal standard (ISTD) (mix of 25 deuterated-PAHs at 50 ng/ml and 8 C13-labeled PCBs at 250 ng/ml) and closed after the addition of a glass fiber filter on top of the cell. Two cycles were run using dichloromethane as solvent and the following extraction conditions: temperature 125 °C, pressure 10 mPa, oven heat-up time 6 min and static time 5 min, flush volume 60% . The extract was transferred into pre-rinsed (acetone and hexane) 100 mL rounded flask and first evaporated using a Rotavap at a pressure of 695 mPa (temperature 40 °C and rotation 100 rpm) to a volume of around 1 mL. Then, it was evaporated to near dryness (20 μL) under a gentle stream of nitrogen before reconstitution in 500 μL of isooctane.

2.3.2 Analysis by GC-MS/MS

Gas chromatography- tandem mass spectrometry (Thermo Scientific TRACE 1310 TSQ Quantum XLS Ultra) with helium (99.999% purity) carrier gas was used for PCBs and PAHs analysis. Quantification was achieved using an 6-point internal standard calibration curve with 14 PAHs (ranging from 4.6 to 700 ng/ml) and a 5-point internal standard calibration curve with 10 PCBs (ranging from 1 to 150 ng/ml). The results for PCBs and PAHs analyses are expressed in $\mu g kg^{-1}$ of dry weight. LOQs vary between 0.01 and 8.1 ng/g for PAHs and range from 0.4 to 0.6 ng/g for PCBs. More details can be found in appendix D.

Total PCBs was estimated by calculating the sum of 7 selected PCBs (28, 52, 101, 118, 138, 153 and 180) multiplied by a correction factor of 4.3 (FOEN, 1998).

To identify the sources of PAHs, the ratio of low molecular weight to high molecular weight PAHs (LMW/HMW) was used. A fraction lower than one suggest that the source is pyrogenic (incomplete combustion), while a ratio higher than one points to a petrogenic source (from coal, coal tar, petroleum and various refinery products). When possible the following ratios were also employed to determine PAHs origin:

- $Fluo/(Fluo+Pyr)$: fluorene divided by the sum of fluorene and pyrene
- $IDP/(IDP+BghiP)$: indeno(1,2,3-cd)pyrene divided by the sum of indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene
- $BaA/(BaA+Chry)$: benzo(a)anthracene divided by the sum of benzo(a)anthracene and chrysene

2.4 Analysis of tire related compounds in environmental samples

2.4.1 Water samples

The following tire additive chemicals were measured in water samples by LC-MS/MS with direct injection and pre-concentration on solid phase extraction (SPE): 1-3 diphenylguanidine (DPG), 2-2' dithiobis-benzothiazole (MTBS), 2-aminobenzothiazole (2-ABTH), 2-Hydroxybenzothiazole (2-HBTH/ 2-OHBT), 2-Mercaptobenzothiazole (S-BTH/ 2M-BTH), 2-Methylthiobenzothiazole (MTBT/ 2MT-BTH), Aniline (AN), Benzothiazole (BT/BTH), cyclohexylamine (CHA), N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) and N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine-quinone (6PPD-Q).

Solid phase extraction

The extraction protocol was tested and adapted from Rauert et al., 2022. Details about the recovery tests are given in Appendix F. 50 μl of deuterated internal standards (782 ng/ml 6PPDQ-d5, 9135 ng/ml BT-d4, 751 ng/ml DPU-d10 and 635 ng/ml Aniline-d5) were spiked in pre-filtered (0.45 μm) water samples (about 100 mL total volume). Oasis HLB cartridge were conditioned with 2 mL methanol and equilibrated with 2ml milliQ® water on the vacuum manifold. Cartridges were then loaded with 100 ml of water sample and with 1 ml of milliQ® water. The cartridge was allowed to dry for 30 minutes. 14 ml of methanol was applied as organic elution solvent and collected in tubes. Extracts were reduced to 20 μl under nitrogen and filled with methanol to make up to a final volume of 250 μl. The final sample volume was diluted twice with the LC-MS/MS eluent. Method blank consisting of 100 mL of MilliQ, extracted following the same protocol, was included in the analysis batches to assess the samples contamination.

LC-MS/MS analysis

Analysis was performed on a liquid chromatography-mass spectrometry (LC-MS/MS Waters Acquity Xevo TQ MS). Quantification was achieved using an 6-point internal standard calibration curve for each compound (ranging from 0.4 to 430 ng/ml). Calibration curve has been processed twice in the batch, before and after environmental samples, and eluents were analysed in between to ensure stability of the instrument.

2.4.2 Soil and sediment samples

Pyr-GC-MS

The soil and sediment samples were analysed for synthetic and natural rubber on a multishot microfurnace pyrolyzer (EGA/PY Frontier 3030D) coupled with a GCMS (Agilent 8890).

The rubber of commercial tires is composed of a range of different formulations and % contents of styrene butadiene rubber (SBR), butadiene rubber (BR) and natural rubber (NR). As such, a range of common pyrolysis products of SBR, BR and NR together with pyrolysis products of tire additives were analyzed to detect tires (see table 3).

A soil and sediment sample mass of 20 mg was selected based on literature values ranging from 2 to 50 mg (Eisentraut et al., 2018; K. Unice et al., 2019). For each soil and sediment, triplicates were analysed and blanks consisting of empty pyrolysis cups were processed every 6 samples.

Details about the previously conducted tests and pyr-GC-MS parameters are given in appendix F.

Table 3: Pyr-GC/MS markers monitored for tires particle detection in soil and sediment sample

Tread polymer	Pyrolysis marker	Mode [b]	Monitored ions (m/z) [a]	Retention time (min)
BR, SBR	4-Vinylcyclohexene (4-VCH)	PY	**54**, 79, 108	6.01
	4-Phenylcyclohexene (4-PCH)	**PY**/ TD	**158**, 91, 54	91/104
SBR	Styrene (STY)			
NR	Dipentene (DP)	PY/**TD**	**136**, 68, 93	11.65/10.80-11.60

(a) Markers of tire rubber

Pyrolysis marker	Mode [b]	Monitored ions (m/z) [a]	Retention time (min)
Benzothiazole (BTH/BT)	**PY**/ TD	**135**, 69, 108	17.50/17.30
2-Methylthiobenzothiazole (MTBT/ 2MT-BTH)	TD	**181**, 108, 148	26.55
2-Mercaptobenzothiazole (S-BTH/ 2M-BTH)	TD	**167**, 109, 123	30.35
N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)	TD	**268**, 211, 253	32.90
2,2,4-Trimethyl-1,2-dihydroquinoline (TDQ)	TD	**158**, 143, 173	23.35

(b) Markers of tire additives

[a] *Monitored ions in bold are target ions used for quantification, the other ions are only diagnostic ions.*

[b] *When two pyrolysis modes are specified, the best one is in bold type.*

2.5 Non-target screening of soils and sediments

2.5.1 Extraction by ASE

Organic compounds covering a broad range of polarities ($\log K_{ow}$ values ranging from -1.43 to 5.31, see appendix G) were extracted from soil and sediment samples by accelerated solvent extraction (ASE), according to the protocol adapted from Du et al., 2017 by the GR-CEL technicians. A glass fiber filter was introduced at the bottom of pre-cleaned 22mL ASE cells (20 minutes in ethanol and ultrasonic bath). They were sequentially filled with florisil 60-100 mesh (1 g), silica gel 60 (3 g), basic alumina (5 g) and a mix of hydromatrix with 500 mg of each soil and sediment. The ASE cells were filled with hydromatrix until 0.5cm of the top, spiked with 25 μL of internal standard (ISTD) (mix of 23 deuterated- and/or C13- compounds covering a broad range of polarity) and closed after the addition of a glass fiber filter on top of the cell. Two cycles were run using methanol as solvent. Extraction conditions were as follows: temperature 100 °C, pressure 1500 psi, oven heat-up time 6 min and static time 5 min, flush volume 50% .

The extract was transferred into pre-rinsed (acetone and hexane) 100 mL rounded flask and evaporated using a Rotavap at a pressure of 218 mPa (temperature 40 °C and rotation 100 rpm) to a volume of around 1 mL. Then, it was filtered (0.2 μm PTFE seringue) and evaporated to 250 μL under a gentle stream of nitrogen.

Before analysing each sediment and sample in triplicate (33 extracts in total), a recovery test was conducted with one sediment sample (MB2) spiked with 25 μL of a mix of 23 internal standards at $\pm 1 ng/mL$. It gave suitable recoveries for most compounds with an overall mean of 53±35% (see Appendix G for more details) for $\log K_{ow}$ ranging from -1.43 to 5.31. Internal standard recoveries were computed for each soil and sediment sample. Three method blanks, obtained by following the same ASE protocol but without the addition of a sample, was done in between environmental samples.

2.5.2 LC-HRMS analysis

Samples were analysed with LC-HRMS Orbitrap (LC: Vanquish, Thermo Fisher Scientific / High resolution mass spectrometer: Orbitrap Exploris 120, Thermo Fisher Scientific/ Mass resolution: High mass resolution up to 120,000 (FWHM) at m/z 200 over the mass range m/z 40–3000). Method blanks were processed at the beginning of the batch and blanks, consisting of LC-HRMS eluent, were processed every 10 samples. Besides the realisation of a non target screening, quantification was achieved for some compounds (listed in appendix G) using an 6-point internal standard calibration curve with concentrations ranging from 0.5 to 900 ng/ml. Calibration curves were analysed twice, before and after environmental samples.

2.5.3 Data analysis

Results were analysed with Compound Discover, a commercial software package developed by Thermo Fisher Scientific for mass spectrometry data analysis of small molecules. The workflow template chosen for the analysis of the raw data is "Environmental Unknown ID w Database Searches and Molecular Networks", showed on Figure 6.

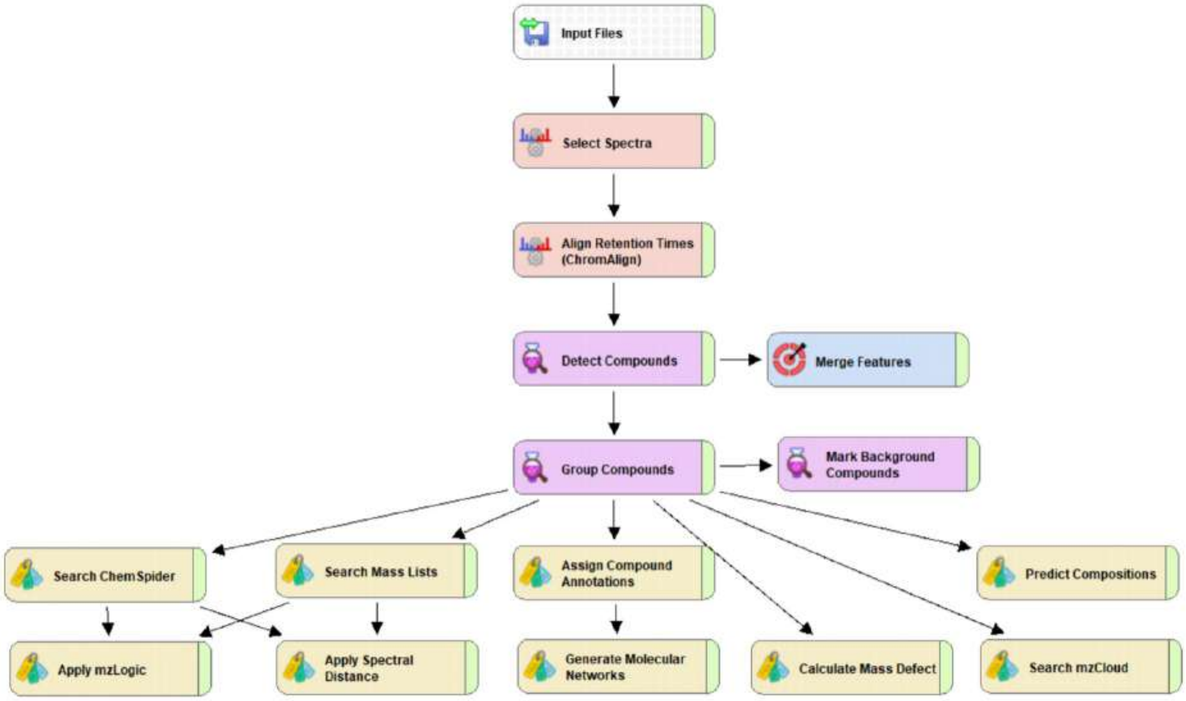


Figure 6: workflow template "Environmental Unknown ID w Database Searches and Molecular Networks" from Compound Discover (Thermo Fisher Scientific).

The following steps are carried out in the NTS data analysis workflow:

1. Data acquisition and curation
    - Peak picking
    - Grouping isotopologues and adducts of the same component in features
    - Hide chemical background
    - Retention time alignment
    - Peak selection based on different criteria: high peak intensity, used as a proxy for high concentration/ low noise level/ high quality peak/ occurrence of the peak
2. RT and MS1 identification
    - Determine elemental composition based on high-resolution full MS isotopes and MS/MS spectra
    - Database search based on accurate mass (or elemental formula) from ChemSpider libraries
    - Suspect screening based on accurate mass (with or without RT) from mass lists
3. MS2 identification
    - MS/MS database search (mzCloud, mzVault)
    - Mz Logic data analysis algorithm: in silico fragmentation tool used to rank order structure candidates from ChemSpider and mass list matches

Almost every node of the workflow can be adapted by changing several parameter values. The most important variables for this study were adjusted as follow:

- Detect compounds node
  S/N threshold of 3
  Min. peak intensity of 1’000’000
  Peak quality factor >6
  Peak detected in at least 2 files
- Search ChemSpider node
  Databases: EAWAG Biocatalysis/Biodegradation, EPA DSSTox, EPA Toxcast, Drugbank, ACToR and FDA UNII – NLM
- Search Mass Lists node
  Mass lists: EFS HRAM Compound database (1’634 semi-relevant compounds), self-made database (61 relevant compounds being either pesticides/ herbicides/ tire additive/ pharmaceutical derived product/ hormone or industrial chemical, including among others dicofol, methamidophos, methomyl, carbofuran, dimethoate, ethoprophos, which are pesticides known for their use in the region of Dakar (A., 2010) as well as dioxin and furan)

- Mark Background Compounds
  Max. Sample/Blank of 5

To evaluate the quality of the predicted compositions match, various parameters are calculated by the software, of which sfit(%), which "Displays the similarity score between the theoretical and measured isotope patterns as a percentage".
The levels of confidence proposed by Schymanski et al. were used to describe how certain the identification was.

Nontarget/levelOfconf.jpg

Figure 7: Identification confidence levels proposed by Schymanski et al. (reproduced from Schymanski et al., 2014)

To be able to deal with the large amount of data resulting from the workflow and to focus on an acceptable number of identification proposals, some filtering criteria had to be chosen. The compounds to be looked at in priority were selected based on the following objectives (corresponding filtering criteria is given in brackets):

- Concentrate on potential contaminants (mass list search has at least one match)
- Have a satisfactory degree of identification confidence (mass tolerance ± 3ppm, Sfit (MS1) > 50 %, full match for predicted composition)

- Ensure the presence of the compound in the sample by having peaks of good quality in at least 2 of the triplicates (area has any value in at least 2 files/ peak rating is above 6 in at least 2 files)
- Guarantee no contamination from the samples pre-processing steps (area has no value in control files)

2.6 Physicochemical analysis on soil, sediment and water samples

Total organic carbon and total carbon analysis on soil and sediment were performed by the GR-CEL technicians (EPFL) on a DOC/TOC analyser (Elementar Vario TOC Cube).
Temperature, pH, conductivity, phosphates, nitrates and turbidity were measured by the waste water treatment laboratory (LATEU) of the University Cheikh Anta Diop of Dakar (UCAD).

2.7 Parameters of sediment and soil quality assessment

Geo-accumulation index and enrichment factor

There are numerous geochemical assessment techniques allowing to determine whether sediments are enriched by anthropogenic activity and whether they are a potential threat for local fauna. Here, we chose some of the commonly used parameters to assess sediment and soil pollution. To quantify the extent of anthropogenic trace metals contamination associated with the sediment, the geoaccumulation index (I_{geo}) introduced by Müller (1979) was used. I_{geo} is defined by the following equation:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 B_n} \right) \tag{1}$$

where C_n is the concentration of metal examined in sediment samples, B_n is the concentration of metal in geochemical background and 1.5 is a factor used to include possible variation of background values due to lithogenic effects (Müller, 1979). The index of geoaccumulation consists of seven grades, or classes ranging from unpolluted to extremely polluted. Since no regional backgrounds were available for the region of Dakar, the background concentrations values used in this project were the metal concentrations of the upper crustal material, showed in Table 4 (Taylor et al., 1995). Soil and sediment that develop above the crustal material should have, as a first approximation, a metal content of the same magnitude. These values were also compared to a reference soil sampled 2.5 km away from Mbeubeuss by Niang et al., which has also, according to the same author, similar geochemical background than soils coming from the peri-urban *Niayes*.

Table 4: Background concentrations in the upper crust material (Taylor et al., 1995) and in the reference sample (Niang et al., 2012).

Concentration [mg/kg]	Pb	Cd	Fe	Cu	Ni	Zn	Ti	Cr	Mn	Co	As	Mo	V
Bn (Taylor et al., 1995)	20	0,098	35 000	25	20	71	3 000	35	600	10	1,5	1,5	60
MB-ref (Niang et al., 2012)	5	<1		7	<2	15		15			<3		

The enrichment factor was calculated according to Equation (2) for determining how much the presence of an element in sediments has increased because of human activity, relative to its average natural abundance.

$$EF = \frac{C_n/C_{Fe}}{B_n/B_{Fe}} \tag{2}$$

Where C_n/C_{Fe} is the ratio of the concentration of metal n to iron. Normalisation to a conservative element as Fe or Al is commonly employed in order to compensate for the natural variability of the metals in the sediments, as influenced among other by differences in mineralogy, granulometry and organic matter (Moez et al., 2018, Loring, 1991, Daskalakis et al., 1995). Iron was chosen as the element of normalization because natural sources (98%) vastly dominates its input (Kamau, 2002). Moreover Bodin, N'Gom-Kâ, et al. showed that Al, Li and Fe are considered as characteristic of the geological matrix in Southern West Senegal. Enrichment factors were interpreted based on previous studies with classes ranging from no enrichment to extremely severe enrichment (Moez et al., 2018).

Sediment quality guidelines

Numerous sediment quality guidelines (SQGs) have been developed to assess the quality of freshwater and marine ecosystem sediments, by comparing pollutants concentrations, including heavy metals, PCBs and PAHs, with reference values. In most cases, two values were defined, corresponding to *"three ranges of chemical concentrations; those that were randomly, occasionally, and frequently associated with adverse biological effects"* (Long et al., 1998; MacDonald et al., 1996). Smith et al. (1996) proposed two effect level to predict the potential biological threat to benthic organisms in freshwater ecosystems :

- TEL: threshold effect level (level unlikely to be associated with adverse biological effects)
- PEL: probable effect level (high likelihood of toxicity on sediment dwelling-organisms)

These guidelines were developed for 23 chemicals based on empirical data compiled from field and laboratory studies performed in North America. These data indicated that no toxic effects were observed in more than 90% of cases in which pollutants concentration were below TEL. The reliability of the PELs was generally lower than that of the TELs, i.e. toxic effect occurred in more than 50 % of cases in which pollutants values exceeded the PEL for only 7 of the 23 substances. Nevertheless, the authors suggest that they are adequate toxicity indicators given their comparability with other SQGs. The development of the Canadian Sediment Quality Guidelines for the protection of aquatic life (Canadian Council of Ministers of the Environment, 2001) for freshwater ecosystems was based on the above mentioned work (Smith et al., 1996) and led to the definition of two levels to predict the incidence of toxic effect:

- Interim freshwater sediment quality guidelines (ISQGs; dry weight),
- Probable effect levels (PELs; dry weight)

Macdonald et al. (2000) developed consensus-based SQGs for freshwater sediments based on an in-depth review of previously published values. For each contaminant of interest, they proposed two levels to determine whether sediments could be toxic :

- TEC: threshold effect concentration (basis for predicting the absence of toxic effect)

- PEC: probable effect concentration (basis for predicting sediment toxicity)

In this project, heavy metal, PAHs and PCBs concentrations in sediment were compared to the previously mentioned guidelines to determine their toxicity.

Soil guidelines

As there is no legislation about soil quality in Senegal, we will rely on guidelines values developed by two countries to evaluate soil quality:

- Guideline values, investigation thresholds and remediation values defined in the Swiss legislation (Osol, 1998).
- Soil quality guidelines for the protection of environmental and human health for agricultural and industrial soils (Canadian Council of Ministers of the Environment, 2001).

The guidelines values used in Switzerland correspond to the *"level of severity of the damage beyond which, according to the state of science or experience, the fertility of the soil is no longer guaranteed in the long term* "(Osol, 1998). Fertile soil means, among other things, a soil with a typical structure that allows normal development of plants, produces food and fodder that does not threaten the health of humans or animals. Furthermore, inhalation or ingestion of a fertile soil does not present health risk for human and animal.

2.8 Parameters of water quality assessment

The guidelines chosen for the evaluation of drinking water quality are the ones developed by the WHO (2017). Pollutants concentration in surface water were also compared with the environmental quality standards (EQS) for priority substances and certain other pollutants, developed by the European Union with the aim of achieving a good water surface chemical quality (EU, 2013). The objective of the directive is to prevent acute and chronic toxic effect on aquatic organisms, to preserve ecosystems and biodiversity and to avoid health risk for humans. They defined two values:

- AA-EQS: EQS expressed as annual average value
- MAC-EQS: EQS expressed as maximum allowable concentration

Due to the lack of data to calculate the average annual concentration, MAC-EQS, which are significantly lower, were used as reference values. In the EU directive, no EQS is given for arsenic despite its proven toxicity. Therefore, the Environmental Guide Value (VGE), derived by the National Institute for the Industrial Environment and Risks (INERIS) following the same methodology as for the EQS derivation, was employed (INERIS, 2015).

2.9 Statistical analysis of data

A hierarchical clustering with Ward's method, as well as principal components analysis (PCA) were performed using R (4.1.2 GUI 1.77 High Sierra build) based on the available data (physico-chemical data, heavy metal, PAHs and PCBs) in order to explore relationships among samples and variables. Prior to analysis, data were centered and scaled in order to give descriptors the same weight, although their initial variance was different.

Data having different units in soil/sediment and water samples (for example heavy metals) were separately normalized, therefore direct comparison between a value in water and sediment is not possible. The clustering was done on the Gower distance matrix (dissimilarity matrix) whereas PCA is by definition done on a Pearson correlation matrix. Different criteria were considered to define the ideal group number resulting from the dendrogram; the graph of fusion levels, the spearman's rank correlations graph and the silhouette graph.

Pearson correlations between variables were also calculated with R, excluding sampling point Mb1rw, which is not comparable to the superficial water and groundwater due to its different nature. The function t.test from Excel was used to understand whether differences between variables were statistically significant, based on the Student's t-distribution, with an unequal variance T-test. The one-factor ANOVA was also used in some cases to determine if data means were significantly different between the sites and type of sample, followed by Tukey's range test to perform multiple pairwise comparisons between groups. When data distribution was not normal, the Krustal Wallis test, followed by the Dunn test, were employed instead of the two tests mentioned just above. Boxplots, heatmaps, pies and histograms were created thanks to R or Excel.

3 Results and discussion

3.1 Physicochemical characteristics of environmental samples

Table 5: Physicochemical characteristics of soil and sediment samples.

Site	Sample	T[°C]	pH	Conductivity [$\mu S/cm$]	TC [%]	TOC[%]	Distance to the landfill/ road [m]
Mbeubeuss	MB1s	25,4	6,95	20	0,314	0,204	0
	MB2sed	25,5	6,85	690	0,168	0,118	150
	MB3sed	25,8	7,43	2020	2,019	0,861	320
	MB5sed	25,6	7,79	20	<LOQ	0,082	100
	MB7sed	25,8	7,79	140	0,433	0,348	420
	MB9s	25,1	7,62	30	0,535	0,471	0
Technopole	TEP1sed	26,6	7,23	5060	3,519	2,446	1170
	TEP3sed	26,3	8,69	810	1,976	0,549	645
	TEP4sed	26,3	8,14	940	2,240	0,672	300
	TEP5.1s	25,6	8,28	200	0,239	0,173	5
	TEP5.2s	26,0	7,42	240	0,504	0,371	5

Table 6: Physicochemical characteristics of water samples.

Site	Sample	T[°C]	pH	Conductivity [$\mu S/cm$]	Turbidity [NTU]	Nitrates [mg/L]	Phosphates [mg/L]	Distance to the landfill/ road [m]
Mbeubeuss	MB2sw	25,7	6,95	9040	13,10	1,8	0,76	150
	MB3sw	25,7	7,19	9670	51,44	47,0	1,78	320
	MB4gw	25,8	6,60	9090	19,98	156,9	0,15	260
	MB5sw	25,8	6,92	2220	6,04	90,8	5,39	100
	MB6gw	25,7	6,70	4260	14,67	126,2	0,41	60
	MB7sw	25,8	6,86	2970	5,13	167,6	2,13	420
Technopole	TEP1sw	27,1	8,14	8360	39,90	1,2	4,55	1170
	TEP2sw	27,4	8,38	8330	41,50	1,1	4,47	1000
	TEP3sw	27,3	8,55	8370	37,81	1,1	4,52	645
	TEP4sw	27,5	8,66	8370	30,83	1,4	4,45	300

Nitrate concentration in superficial water coming from the sampled ponds of Mbeubeuss and in groundwater are above the WHO guideline value of 50 mg/l in most cases (4 out of 5), with values ranging from 47 to 167,6 mg/L. This correlates the final report of Mbeubeuss rehabilitation plan, which also put in evidence high concentrations, with measurable values ranging from 0,62 to 370 mg/l depending on the distance to the discharge (2 to 950 meters) and type of water (superficial and groundwater) (Ministère de l'urbanisme, du logement et de l'hygiène publique et al., 2019). Moreover, the book chapter written by Niang et al. pointed out elevated nitrate concentration ranging between 100 and 450 mg/L in the wellfield of the *Thiaroye* table. The reason for this pollution is related to the infiltration of liquid waste from latrines and leachates from solid waste due to a faulty sewage system and poor solid waste management according to Tandia, 2000. S. Cissé highlights a very irregular spatial distribution of nitrates concentration in the aquifer, which is explainable by the presence of localised sources of emission, highly dependent on population density.

Superficial water from the Mbeubeuss lake (MB2) and Technopole lake have much lower nitrates concentration (1,1-1,8 mg/l). According to Tukey's test (see Figure 45 appendix H), nitrates concentration are significantly different between superficial water from Mbeubeuss ponds and superficial water from Technopole lake (*p-value* of 0.04) as well as between groundwater from Mbeubeuss and superficial water from Technopole (*p-value* of 0.02).

A recent study published by C. Diop et al. revealed however higher levels of nitrate (16,2 mg/L) in the Grande Niaye of Pikine. Nitrate may come from multiple sources such as the application of inorganic or organic fertilizer in the market garden crops areas, the slurry from animal production (in the case of the landfill) or the decomposition of organic substances and wastes. Moreover, their article showed high pH values (> 8.5) in the lakes whereas the pH values found in this study are in most cases between the standard values of 6.5 and 8.5, with the exception of TEP4 whose pH is slightly above.

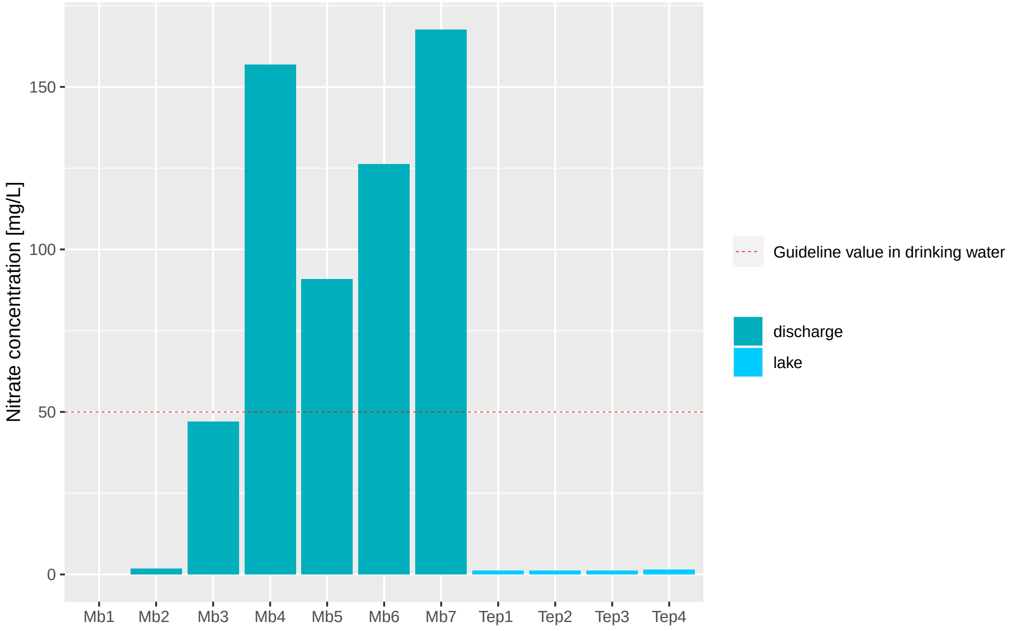


Figure 8: Nitrates concentration [mg/L] in water samples.

Different types of soils and sediments are found around both sites:

1. Ferric arenosols (FAO soil group), which consist of tropical ferruginous sandy soils with little leaching. They have high amounts of iron oxides, low organic content (mean TOC 0,7 %) and acidic pH which can turn into alkaline if irrigated with saline water (mean pH6.8).
2. Hydromorphic soils, which are sandy clay soils with high OM (mean TOC 3-8 %) and high Mg/Ca content.
3. Halomorphic soils, which contains a significant proportion of soluble salts (slightly to fairly saline soils) and ends at the level of the dune cords in the southern part of the *Niayes*.
4. Anthroposols, which are soils profoundly modified or constructed by humans.

According to the detailed urbanism plan of Pikine-Guediawaye 9, TEP5.1 and TEP5.2 are located in a region of hydromorphic soils but they have been so intensely modified by humans through road works and grass planting that they can rather be characterized as anthroposol. The remaining sediment of Technopole (TEP1, TEP3 and TEP4) and all sampling points of the landfill, including soil MB1 and MB9 and sediment MB2, MB3, MB5 and MB7 are in the zone of halomorphic soils. No classification is given for MB2. The type of soil given by the map seems to be imprecise, given that physico-chemical parameters do not correspond to expected values, i.e. high TOC for hydromorphic soils and high conductivity for halomorphic soils.

In addition to that, Niang et al. state that the soils to the northwest of the landfill are all ferruginous soils with the most distant (about 300 m) having a hydromorphic character. According to that, Mb1/MB2/MB3/ MB5/ MB9 should be ferruginous soil or sediment, variably affected by hydromorphy. In the area of MB7, they found either ferruginous soil or organic gley.

By looking at the samples, we can say that almost every sample has a silty to fine sandy granulometry, except sediment TEP1 whose grain size is much finer (clay or silty). MB9 and especially TEP1 have a brown red color. MB5 also contrasts from other samples due to its medium sandy granulometry and a very light yellow color.

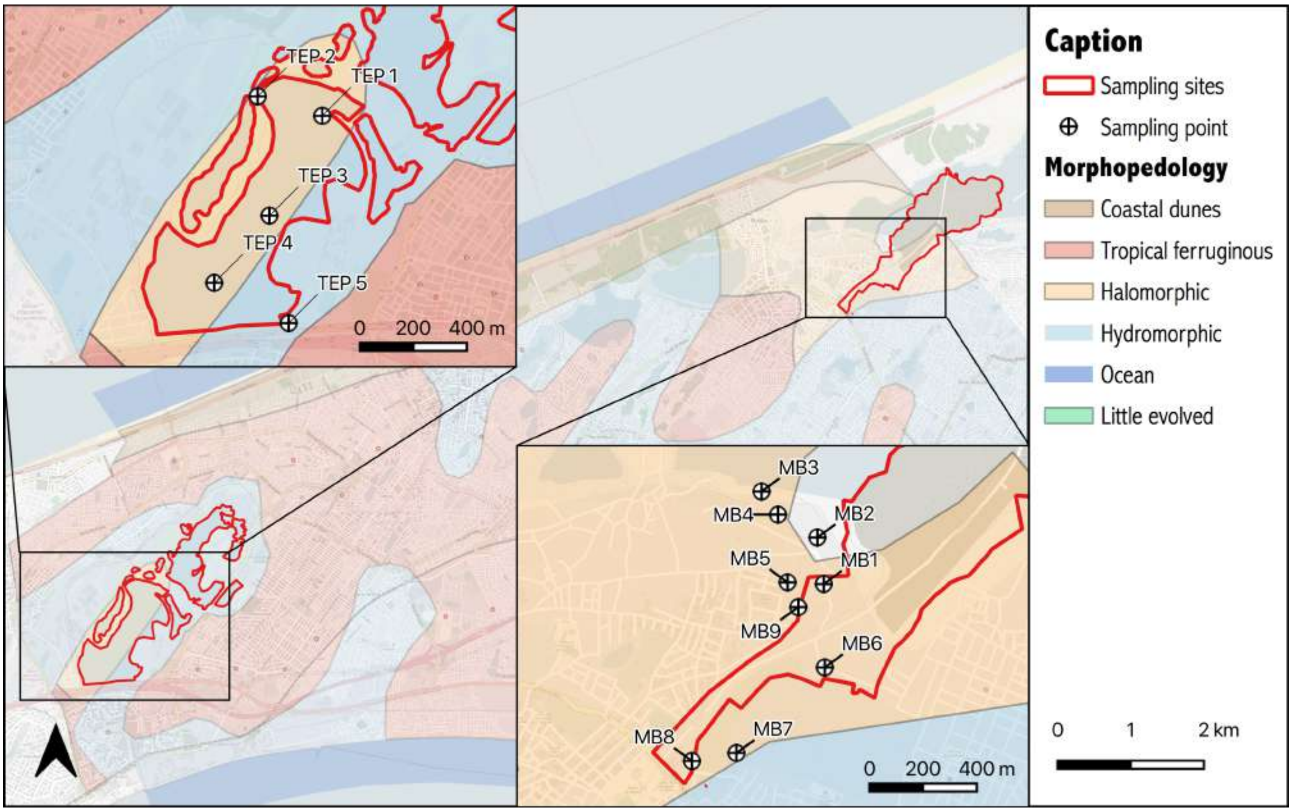


Figure 9: Morphopedology of both sampling sites, according to the detailed urbanism plan of Pinkine-Guediawaye.

3.2 Heavy metals in environmental samples

Figure 11 shows the results obtained for heavy metal concentrations exceeding the reference limits (i.e. guideline value in drinking water or threshold effect limit for sediment) as well as for zinc, whose content is high in tires (1% wt. Councell et al., 2004). Normalized concentrations for each metal are represented with a heatmap on Figure 10.

Heavy metal concentrations were also plotted as a function of the distance to the nearest point of the landfill (0 to 420 meters) but no particular trends were observed. Furthermore, 84% of the correlations values were between -0.5 and 0.5, with only the following metals being outside this range: Mn (0.62) and Co (0.87) in water samples and As (0.78) and Mn (0.79) in soil and sediment samples. These values indicating either a low degree of correlation or a high positive correlation (meaning that the the farthest points have the highest concentrations) suggest that there is no clear linear relationship between metal pollution and the landfill (see Appendix B).

Heavy metals can accumulate in road dust through atmospheric deposition and be further transported by runoff water, however, little to no influence of the Technopole road (situated at 5 to 1200 meters) on metal concentration was observed either. Moderate to high positive correlations (>0.75) were obtained for almost all metals in soil/sediment of Technopole, with the exception of a weak negative correlation for Mo (-0.41) and a medium negative value for Cd (-0.75), indicating that only Cd is likely to originate from the road. Water showed also medium to high positive correlations (>0.44) for nearly all metals (except Cr), meaning that the most distant points had the highest concentrations and implying that the road is not the main metal pollution source. Chrome was however strongly negative correlated (-0.98) to the distance to the road and its concentration may therefore be influenced by traffic dust, whose source of chrome include fossil fuel burning, metallic corrosion and paint abrasion (Bisht et al., 2022).

The multiple sources of contamination (see Table 2) and the geographical complexity of both sites make the identification and separation of pollution causes difficult, especially with so few sampling points. The influence of the landfill on groundwater could be analysed based on transects defined thanks to piezometric maps (S. Cissé, 2000; Tandia, 2000) to take into account the complexity of the groundwater flow as suggested by Niang et al., but, in this project, there are too few groundwater sampling points. More data is needed to quantify the impact of the landfill and its involvement on the observed contamination levels.

Metal concentrations are generally higher in sediments and soil than in water by about three order of magnitude, as can be seen by the units of the graph (i.e. concentrations are given in mg/kg for sediment/soil and in $\mu g/L$ for water). Their poor solubility in water encourages their accumulation in sediments, where they can occur in different forms such as organic complexes, inorganic complexes with dissolved anions and free hydrated metal ion (Kalis, 2006).

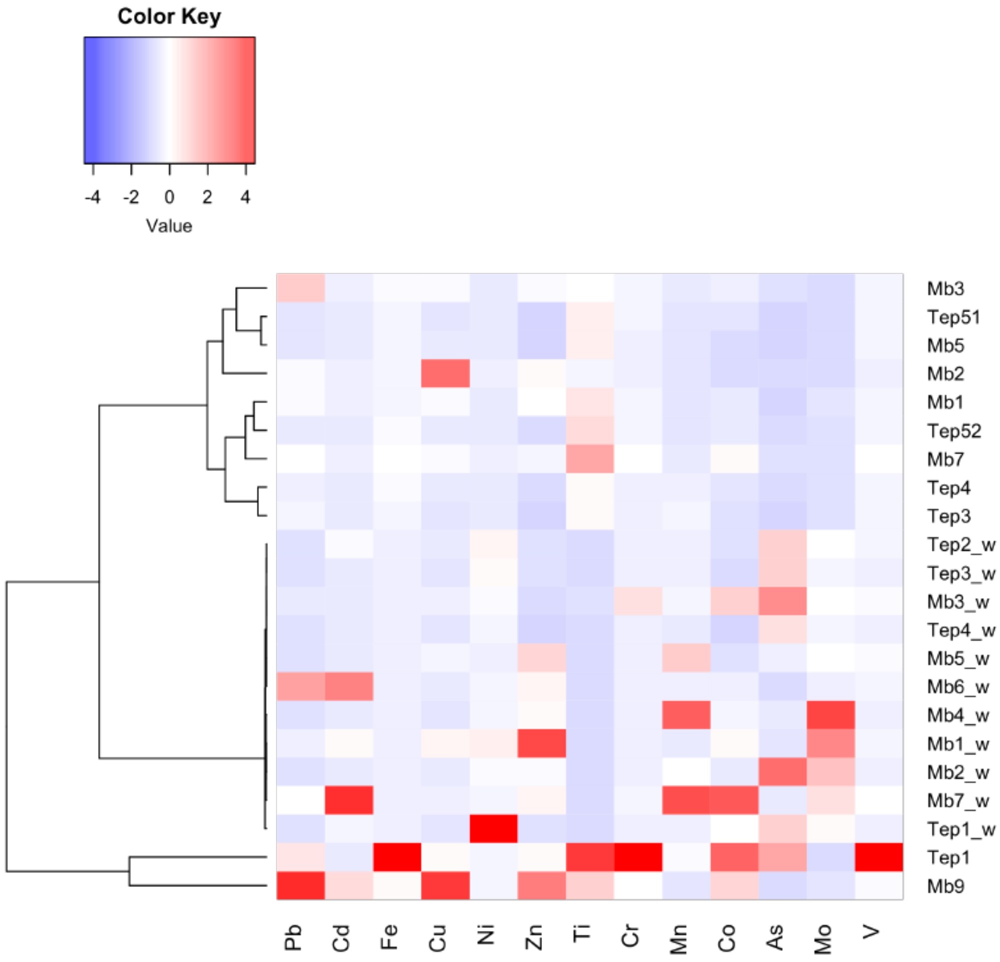


Figure 10: Heatmap of normalized heavy metal data in water, soil and sediment samples with the dendogram from the hierarchical clustering (Ward cluster on Gower distance matrix). Initial units are mg/kg for soil and sediment and $\mu g/L$ for water.

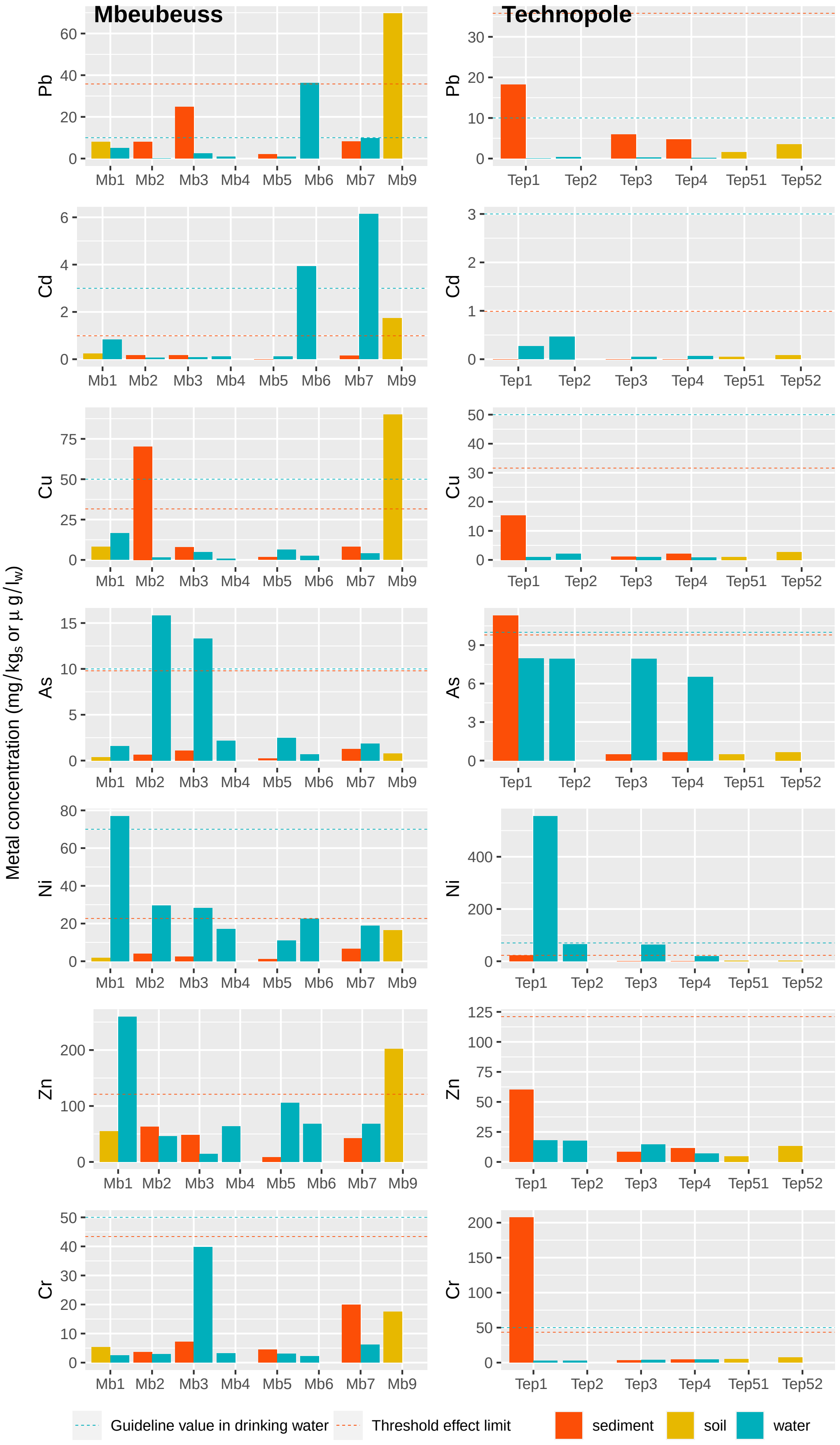


Figure 11: Heavy metal concentrations in sediment, water and soil samples from Mbeubeuss landfill and Technopole lake.

3.2.1 Water samples

Table 7: Mean heavy metal concentrations [$\mu g/L$] in water samples from Mbeubeuss landfill and Technopole (± standard deviation).

Metal mean concentration [$\mu g/L$]	Mbeubeuss				Technopole		WHO guideline value [b]	MAC-EQS/ VGE [c]
	Superficial water[a]		Groundwater		Superficial water			
	(n=4)	std	(n=2)	std	(n=4)	std		
Pb	3,3	±4,7	18,6	±25,1	0,2	±0,2	10	14
Cd	1,6	±3,5	2,0	±2,7	0,2	±0,2	3	0,45[d]
Fe	192,1	±163,9	198,4	±207,3	125,8	±98,4		
Cu	4,2	±1,2	1,8	±1,3	1,3	±0,6	2000	
Ni	21,9	±8,6	19,9	±3,8	176,3	±254,0	70	34
Zn	58,5	±46,1	65,6	±3,1	14,4	±5,1		
Ti	5,8	±9,0	1,0	±0,3	0,7	±0,3		
V	6,9	±2,2	1,9	±1,7	2,1	±0,3		
Cr	13,0	±20,3	2,8	±0,7	3,5	±0,8	50	
Mn	586,5	±645,0	693,8	±857,3	87,4	±16,4		
Co	2,4	±2,7	0,9	±0,2	0,6	±0,6		
As	8,4	±6,4	1,4	±1,1	7,6	±0,7	10	1,37
Mo	4,6	±1,4	8,8	±10,7	2,3	±0,7		

[a] *Rainwater is not considered as an environmental sample and is therefore not included in the mean of superficial water.*
[b] *Cells colored in red means an overcoming of WHO guidelines for safe drinking water (WHO, 2017).*
[c] *Values written in red are above the MAC-EQS or EGV defined by the EU and INERIS (EU, 2013; INERIS, 2015)*
[d] *MAC-EQS of cadmium ranges from 0,45 to 1,5 $\mu g/L$ depending on water hardness.*

Individual concentrations of each sample and boxplots are given in Table 16 and Figure 20, Appendix B.

Mean heavy metal concentrations in water (excluding rainwater sample MB1) follow the order of Mn (408.3 μg/l)> Fe (166.9 μg/l)> Ni (83.3 μg/l) > Zn (42.3μg/l)> Cr (7.2 μg/l)> As (6.7μg/l)> Pb (5.1 μg/l) > Mo (4.5 μg/l)> V (3.9 μg/l)> Ti (2.8 μg/l)> Cu (2.5 μg/l) > Co (1.4 μg/l)> Cd (1.1 μg/l).

In the landfill of Mbeubeuss, five water samples had metal concentration above the recommended values for drinking water (WHO, 2017); Mb1 (rain water standing in a tire with Ni= 0.077 mg/l), Mb2 (superficial water with As= 0,0016 mg/l), Mb3 (superficial water with As= 0,0013 mg/l) Mb6 (groundwater with Pb=0.036 mg/l and Cd=0.004 mg/l) and Mb7 (surface water with Cd= 0.006 mg/l) whereas only the metal content of Tep1 (surface water with Ni=0.556 mg/l) exceed the reference value in the lake of Technopole.

By comparing the metal concentrations with the Environmental Quality Standards, it can be deduced that the arsenic content is too high in all samples with the exception of MB6, as well as nickel content in Tep2 and Tep3 and cadmium content in Mb1 and Tep2. Values that do not meet the guideline value in drinking water are also above EQS.

Sample MB1, consisting of rainwater standing in a tire, has a high zinc content of 259.7 μg/l, which is more than 6 times above the mean of the other samples (42.3μg/l). This can be explained by the fact that Zn is the main heavy metal of tire tread, with a content of 1% wt.(Councell et al., 2004).

Looking at the average values (Table 14), we can summarize the pollution as follow:

- Superficial water from the landfill shows cadmium and arsenic pollution (respectively above the GVDW and VGE)

- Groundwater from the landfill has high concentration of lead (above the GVDW), cadmium and arsenic (above EQS/VGE)
- Superficial water from Technopole contains a high level of nickel (above the GVDW) and arsenic (above VGE)

Student's t-tests revealed that metal concentrations in surface water from Mbeubeuss landfill and from Technopole lake are not significantly different (*p-values* higher than 5% for all metals with the only *p-values* below 10 % being Cu and V). There is also no significant difference between groundwater and superficial water from Mbeubeuss landfill (*p-values* > 0.05 with V the only p-value< 0.1). However, results showed significantly lower arsenic and higher zinc concentrations in Mbeubeuss groundwater than in the lake of Technopole, with *p-values* of respectively 0.03% and 3.7%.

O. Cissé (2018) mentioned that water from the landfill wells was non potable due to contamination in heavy metals and pathogenic micro-organisms. This is consistent with the present study as we found high Pb and Cd content in groundwater sample Mb6, situated at about 60 meter from the landfill. Heavy metals in groundwater from sample Mb4, being further away from the discharge (260 m), were however not above WHO's guidelines values. Niang et al. analysed lead concentration along a transect passing near these two points and had similar results, with slightly lower Pb and Cd values, ranging respectively from 0 to 22 μg/l and from 0 to 1 μg/l for distances between 0 to 450 m.

In the study of rehabilitation of the Mbeubeuss dump site, they analysed chemical water quality but their high quantification limit makes the comparison with the present study difficult (Ministère de l'environnement et de la protection de la nature, 2011). Nevertheless, quantifiable values are of the same order of magnitude for As, Fe, Cr, Mn, Ni and Zn in wells and superficial water situated at similar distances from the landfill.

In the report of Wilson et al. (2006), they sampled and analyzed groundwater from a site located slightly south and east of Lake Mbeubeuss (which is the place chosen to resettle populations affected by a highway construction project) as well as superficial water coming from the lake. They found very high content of zinc (15'400 to 33'200 $\mu g/L$), iron (7'900 to 122'000 $\mu g/L$), lead (100 to 300 $\mu g/L$), a high nitrates concentration (2,75 to 191 mg/l), a high number of fecal coliforms (46 to 6800 UFC/100ml) and high level of conductivity 530 to 4'050 $\mu S/cm($ at 29°C). They did not detect any Ni, Cu, Cd or Cr but this is due to the high quantification limit (10 ug/l) of the analytical methods used by the laboratory, which were above the WHO quality criteria. Values with the same order of magnitude were found in the present study for nitrates and conductivity but metal concentrations are three order of magnitude lower. Nevertheless, such a large metal content was also found at a site located very close to the landfill (2 meter) according to the study of the rehabilitation of the site (ibid.). Theses variations could be explained by a local pollution source or temporal variation.

As in the case of groundwater, Wilson et al. found high concentrations of fecal coliforms (64-178 UFC/100ml), iron (6,35-9,2 mg/l) and zinc (29,8-31,5 mg/l) in the lake of Mbeubeuss. However, they had zero concentrations in nitrates, which is consistent with the low level of nitrates in sample Mb2 coming from the lake.

C. Diop et al. (2019) measured metal concentration from five ponds of Dakar, including the lake surrounding Mbeubeuss and the lake of Technpole (five water samples per site). Their results showed slightly lower values in lead and cadmium and significantly lower iron content in Mbeubeuss: Pb 1.38 $\mu g/l$, Cd 0.22 $\mu g/l$, Fe 1.42 $\mu g/l$ compared to Pb 3.6 $\mu g/l$, Cd 1.44 $\mu g/l$, Fe 168 $\mu g/l$ in this study. Technopole's pond had also slightly lower content of lead and neither cadmium nor iron were detected by their study although we found values above their quantification limits (Pb 0.07 $\mu g/l$compared to Pb 0.21 $\mu g/l$, Cd 0.214 $\mu g/l$, Fe 126 $\mu g/l$ in this study). The natural reserve of Technopole is actually separated in numerous small ponds not directly connected to each other. The differences in metal concentrations may be partly explained by the location of collected water samples, which could come from another pond that the one studied in the current project.
Moreover they analysed liver and flesh from the most consumed fish, called Tilapia, from Technopole and concluded that lead and cadmium concentration did not constitute a risk to human health according to European legislation. M. Diop et al. (2017) obtained similar results, suggesting that no human health risk exist associated to consumption of trace metals via fish and seafood from the Senegalese coast. They found that, for most species and sites studied, concentrations of Cd, Pb, and Hg were below the norms defined by the European Union, with the exception of mussels from Soumbedioune, a market place located northwest of the Technopole and Mbeubeuss sites.

In brief, water from both site has a bad chemical quality due to either high lead, cadmium, nickel or arsenic content and should not be consumed by local population without prior treatment. Indeed, 67% of water samples from Mbeubeuss do not meet the GVDW, while this is the case for only 25% of the samples at Technopole. Moreover, both sites have 100 % of the samples contaminated by at least one heavy metal, according to the EQS/VGE, suggesting a potential threat to aquatic organisms and ecosystems.

3.2.2 Sediment and soil samples

Table 8: Mean heavy metals concentration [g/l] in soil and sediment samples from Mbeubeuss landfill and Technopole (± standard deviation)

Metal mean concentration [mg/kg]	Mbeubeuss				Technopole				TEC[a]	PEC[b]	Osol[c]
	Soil		Sediment		Soil		Sediment				
	(n=2)	stdv	(n=4)	stdv	(n=2)	stdv	(n=3)	stdv			
Pb	38,83	±43,66	10,73	±9,76	2,53	±1,36	9,62	±7,49	35,8	128	50
Cd	0,98	±1,06	0,12	±0,08	0,07	±0,02	<LOQ		0,99	4,98	0,8
Fe	4 166	±3 567	2 670	±2 033	2 108	±550	22 972	±36 383			
Cu	**49,08**	±57,88	22,00	±32,36	1,86	±1,21	6,19	±7,92	31,6	149	40
Ni	9,23	±10,28	3,60	±2,36	2,22	±0,39	8,59	±12,83	22,7	48,6	50
Zn	128,40	±104,13	40,51	±23,21	8,99	±6,14	26,69	±29,15	121	459	150
Ti	191,6	±33,9	152,8	±105,3	160,3	±36,4	269,1	±257,2			
Cr	11,44	±8,66	8,80	±7,53	6,29	±1,61	**71,71**	±117,67	43,4	111	50
Mn	22,72	±7,32	39,10	±29,52	32,05	±4,43	128,39	±24,64			
Co	1,63	±1,26	0,77	±0,59	0,69	±0,12	2,22	±2,90			
As	0,59	±0,30	0,81	±0,47	0,58	±0,13	4,17	±6,20	9,79	33	
Mo	0,62	±0,15	0,09	±0,17	0,42	±0,29	0,22	±0,20			5
V	5,78	±3,26	5,78	±5,87	4,68	±1,41	69,52	±112,8			

[a] *Cell are colored in red if above threshold effect concentration proposed by Macdonald et al.*

[b] *Values are in red if above probable effect concentration proposed by Macdonald et al.*

[c] *Values are in yellow if above the indicative value for soils defined by the Swiss legislation (Osol, 1998).*

Regarding mean metal concentration in sediments, the order is as follow: Fe (8'376.6 mg/kg)> Ti (193.0 mg/kg)> Mn (59.2 mg/kg)> Zn (47.0 mg/kg)> Cr (26.0 mg/kg)> V (23.0 mg/kg)> Cu (18.9 mg/kg)> Pb (14.0 mg/kg)> Ni (5.7 mg/kg)> As (1.6 mg/kg)> Co (1.3 mg/kg)> Cd (0.3 mg/kg)> Mo (0.2 mg/kg).

Three samples were above the threshold effect concentration or probable effect concentration given by Macdonald et al., 2000. Canadian guidelines about sediment quality (Canadian Council of Ministers of the Environment, 2001) and values developed by Smith et al. were also taken into account but led to the same conclusions. Sediment Mb2 has a Cu content (70.3 mg/kg) more than twice above TEC value. Sediment Tep1 had nickel and arsenic concentrations just above TEC (23.4 mg/kg and 11.3 mg/kg respectively) and a chrome content significantly higher than PEC (C_{Cr}= 207.6 mg/kg). This is the reason why the mean chromium concentration in the sediments of the lake is above TEC. Most heavy metal concentrations in sediment Tep1 were higher than in any other sample.

Soil sample MB9 found near a tire dumping site (less than 5 meters away) present also high heavy metal concentration, with lead, copper, cadmium and zinc content above the indicative value of the Swiss legislation (Osol, 1998). The average copper content obtained for Mbeubeuss soil samples is also above the guideline value, although the metal content of soil sample MB1 is much lower.

An assessment of lead exposure in children aged 1 to 15 years neighbouring the Mbeubeuss landfill was carried out in 2012 by Cabral et al. Their results showed very high level of lead (1'129 mg/kg), much higher than the present mean for soil samples (38.8 mg/kg).

In the study conducted by Niang et al., they also showed that soil samples located at less than 50 meters away from the discharge were contaminated in Pb, Cd, Cu and Zn. Beyond this distance, they did not observe any soil pollution presenting a potential threat. The highest concentrations they had were in the case of soil collected at the east, where the discharge is the widest, and at short distances. Values of heavy metal were above Swiss or foreign investigation thresholds. In the area of MB1 and MB9 they measured the concentration of two samples, one of which was very polluted (above the investigation threshold of the Swiss legislation), while the other was very similar to MB9. They also pointed out that informal settlements are getting closer and closer to these areas, where inhalation or ingestion of soil could be a threat for animal and human health.

In the study of the reconversion operation of the Mbeubeuss dump site, they measured heavy metals in a band of approximately 50 meters around the landfill. They found again that some soil samples had heavy metal above the investigation threshold (Pb, Cd) or above the indicative value (Ni, Zn, Cr, Cu) of the Swiss legislation. In addition that, they analysed the metal content of wastes and also obtained very high concentration, especially in Cu (up to 970 ng/kg) and Zn (up to 23 000 ng/kg) (Ministère de l'environnement et de la protection de la nature, 2011).

According to the Student's t-tests, metal concentrations in soils from Mbeubeuss landfill and from Technopole are not significantly different (*p-values* higher than 10%). Regarding sediment samples, there is a significant difference in Mn values between both sites (*p-value* of 0.01), as well as in Cd but at a lower statistical significance (*p-value* of 0.06).

Heavy metal concentration for each sample and boxplots are shown in Table 22 and on Figure 20 in Appendix B.

Table 9: EF and I_{geo} values for heavy metals in sediment and soil.

	Heavy metal concentration [mg/kg]	Technopole					Mbeubeuss					
		TEP1	TEP3	TEP4	TEP5.1	TEP5.2	MB1	MB2	MB3	MB9	MB5	MB7
		sed	sed	sed	s	s	s	sed	sed	s	sed	sed
I_{geo}	Pb	-0,7	-2,3	-2,7	-4,3	-3,1	-1,9	-1,9	-0,3	1,2	-3,9	-1,9
	Cd	-	-	-	-1,4	-0,9	0,6	0,1	0,2	3,6	0,0	-
	Fe	0,3	-5,0	-4,5	-4,9	-4,4	-5,0	-5,3	-4,1	-3,0	-5,7	-3,3
	Cu	-1,3	-5,1	-4,1	-5,2	-3,8	-2,2	0,9	-2,3	1,3	-4,4	-2,2
	Ni	-0,4	-4,9	-4,4	-3,9	-3,6	-3,9	-2,9	-3,6	-0,9	-4,7	-2,2
	Zn	-0,8	-3,7	-3,2	-4,5	-3,0	-1,0	-0,8	-1,1	0,9	-3,7	-1,3
	Ti	-3,0	-5,2	-5,2	-5,1	-4,6	-4,7	-6,0	-5,5	-4,4	-5,0	-3,9
	Cr	2,0	-4,0	-3,6	-3,3	-2,8	-3,3	-3,8	-2,9	-1,6	-3,5	-1,4
	Mn	-2,6	-2,8	-3,1	-5,0	-4,7	-5,0	-5,8	-3,6	-5,7	-6,1	-4,1
	Co	-1,4	-5,0	-4,6	-4,6	-4,3	-4,3	-5,2	-4,2	-2,6	-5,8	-3,2
	As	2,3	-2,2	-1,7	-2,2	-1,7	-2,6	-1,8	-1,0	-1,5	-3,3	-0,8
	Mo	-	-3,1	-2,5	-	-2,4	-2,1	-	-	-1,6	-	-2,7
	V	1,2	-4,5	-4,2	-4,6	-4,0	-4,7	-5,5	-4,6	-3,5	-5,0	-2,6
EF	Pb	0,5	6,1	3,7	1,6	2,4	8,5	10,8	14,6	18,2	3,5	2,6
	Cd	-	-	-	11,4	11,5	49,0	44,1	19,7	92,4	-	10,0
	Cu	0,3	0,9	1,3	0,8	1,5	6,9	76,0	3,7	18,8	2,5	2,1
	Ni	0,6	1,0	1,1	2,0	1,7	2,1	5,5	1,5	4,3	2,0	2,2
	Zn	0,5	2,4	2,5	1,3	2,6	16,4	23,9	8,1	14,9	4,0	3,9
	Ti	0,1	0,8	0,6	0,9	0,9	1,2	0,6	0,4	0,4	1,6	0,7
	Cr	3,2	1,9	1,9	3,0	3,0	3,2	2,8	2,4	2,6	4,5	3,7
	Mn	0,1	4,4	2,7	1,0	0,8	1,0	0,7	1,4	0,2	0,8	0,6
	Co	0,3	1,0	1,0	1,2	1,1	1,6	1,1	1,0	1,3	1,0	1,0
	As	4,1	6,9	7,0	6,6	6,3	5,4	11,9	8,7	2,8	5,3	5,4
	Mo	-	3,7	4,1	-	3,9	7,3	-	-	2,5	-	1,5
	V	1,8	1,4	1,2	1,3	1,3	1,2	0,9	0,8	0,7	1,6	1,6

I_{geo}	
<0	unpolluted
0-1	unpolluted to moderately polluted
1-2	moderately polluted
2-3	moderatey to heavily polluted
3-4	heavily polluted
4-5	heavily to extremely polluted
>5	extremely polluted

EF	
>1	no enrichment
1-3	minor enrichment
3-5	moderate enrichment
5-10	moderately severe enrichment
10-25	severe enrichment
25-50	very severe enrichment
>50	extremely severe enrichment

More than 90 % of I_{geo} values were below 0, meaning that most sampling sites were not polluted by heavy metals. One sampling point in the lake of Technopole (Tep1) had higher I_{geo} values than the two other ones. Its I_{geo} class was moderately polluted for chromium and vanadium and moderately to heavily polluted for arsenic. Soil sample Mb9, which came from a tyre storage area, also had high I_{geo} values. The sample was heavily to extremely polluted in cadmium and moderately polluted in lead and copper.

Moreover, a few I_{geo} classes (5%) indicated no pollution to moderate pollution for Cd (Mb1, Mb2, Mb3, Mb9), Fe (Tep1), Cu (Mb2) and Zn (Mb9).

By comparing the data with the reference soil from Mbeubeuss, which has lower metal concentration than the upper crust material, a few more samples would be classified as moderately polluted: Mb1, Mb2, Mb3. Zinc content is also higher than the control value in several samples.

Enrichment factors allowed to determine if the observed concentrations were likely to have lithogenic or anthropogenic origin. 72 % of the samples showed an anthropogenic minor to extremely severe enrichement in heavy metals (EF>1). The concentrations of V, Fe, Ti and Co for all samples were the only ones to be similar to the levels in the earth's crust or to point to a minor enrichment in the soil ($EF < 3$).

The metal presenting the highest EF values is cadmium, whose values ranged from moderately severe enrichment (MB7) to extremely severe enrichment in sample Mb9.

Sediments and soils coming from Technopole sampling site were generally less enriched than Mbeubeuss landfill with respectively 80% and 63% of values below 3 (no enrichment to minor enrichment). Indeed, only As and Mo had moderate to moderately severe pollution in all samples located in the reserve. Some isolated samples showed moderate to moderately severe enrichment in Pb, Cr and Mn. Besides cadmium contamination in Mbeubeuss landfill, copper showed also enrichment ranging from minor to extremely severe in Mb4. EF values of As, Zn and Pb ranging from 3 to 25 in at least 5 samples from Mbeubeuss (out of a total of 6) also suggest they have anthropogenic origin. EF of Mo, Cr and Ni were lower, with no more than three samples having values between 3 and 5 and one sample having values between 5 and 10.

3.2.3 Tires samples

The heavy metal content of tire samples coming from the discharge and its comparison to CMTT, TRWP and TP are shown in Appendix B.2. Briefly, heavy metal composition of tire samples from the discharge very slightly differ from CMTT. This could be partly due to the aging of MB samples through environmental processes and/or initial variations in tires' composition.

3.3 PAHs and PCBs in soils and sediments

Table 10: Mean PAHs concentration [ng/g] in soil and sediment samples from Mbeubeuss landfill and Technopole.

PAHs mean concentration [ng/g]	Mbeubeuss				Technopole				TEC[a]	PEC[b]
	Soil		Sediment		Soil		Sediment			
	(n=2)	Std	(n=4)	Std	(n=2)	Std	(n=3)	Std		
Antracene	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	57,2	845
Benzo(a) anthracene	0,00	0,00	0,05	0,11	0,00	0,00	0,20	0,35	108	1 050
Benzo(a) pyrene	0,00	0,00	0,50	1,00	0,00	0,00	1,71	2,96	150	1 450
Benzo(b) fluoranthene	0,24	0,17	0,08	0,10	0,08	0,11	0,18	0,31		
Benzo(e) pyrene	0,00	0,00	0,44	0,87	0,00	0,00	1,64	2,85		
Benzo(g,h,i) perylene	0,00	0,00	11,18	12,92	0,00	0,00	18,34	31,77		
Benzo(k) fluoranthene	0,00	0,00	0,00	0,00	0,00	0,00	0,04	0,07		
Chrysene	0,73	0,42	0,29	0,28	0,18	0,25	0,57	0,65	166	1 290
Dibenzo(a,h) anthracene	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	33	
Fluoranthene	1,12	0,72	0,61	0,35	0,61	0,40	0,82	0,69	423	2 230
Fluorene	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	77,4	536
Indeno(1,2,3-cd) pyrene	0,00	0,00	0,00	0,01	0,00	0,00	0,01	0,02		
Phenanthrene	21,81	10,34	17,44	11,73	11,26	1,25	16,14	8,63	204	1 170
Pyrene	0,74	0,43	0,52	0,35	0,74	0,52	0,62	0,52	195	1 520
Σ14 PAHs	24,52	12,08	30,78	14,48	12,49	2,53	40,08	48,79		
Σ13 PAHs [c]	24,52	12,08	30,78	14,48	12,49	2,53	40,07	48,78	1 610	22 800

[a] *Cell are colored in red if above threshold effect concentration (TEC) proposed by Macdonald et al.*

[b] *Values are in red if above probable effect concentration (PEC) proposed by Macdonald et al.*

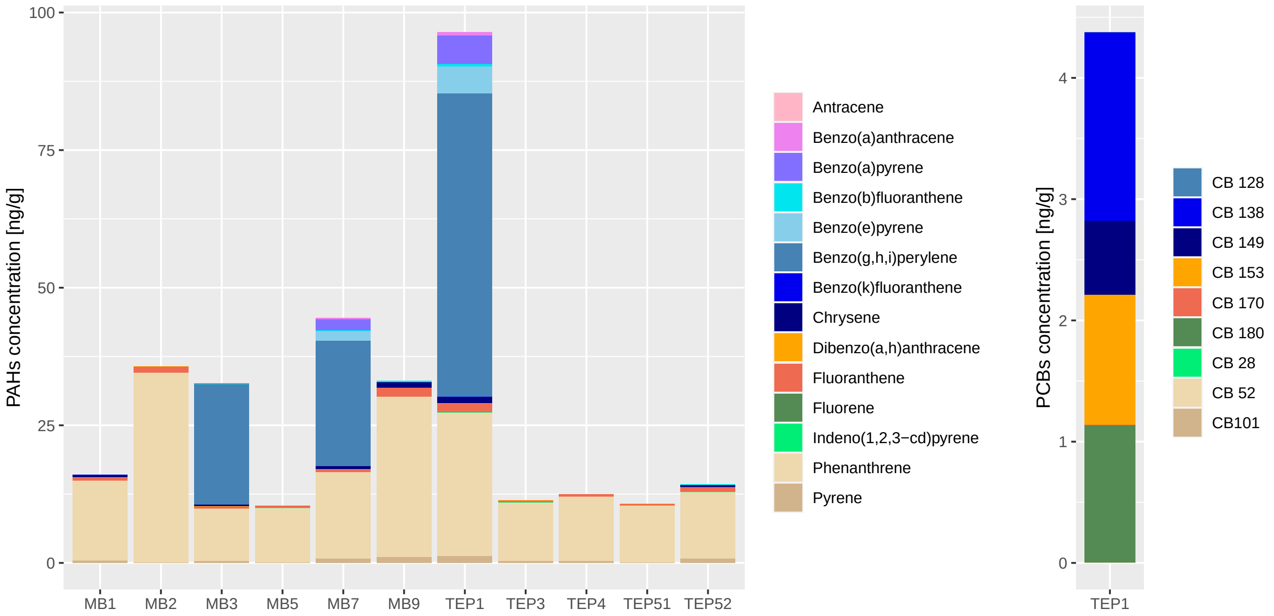
[c] *Indeno(1,2,3-cd)pyrene is not included in the sum.*

Detailed concentrations for each sample are given in Appendix D.

The level of contamination and the distribution of PAHs and PCBs are not homogeneous through the two sampled sites (see Figure 12 and Table 10). All the tested sediments and soils presented detectable amount of PAHs with the sum of Σ14 PAH ranging from 10.41 $\mu g/kg$ to 96.42 $\mu g/kg$. Of the 14 PAHs tested, only 12 PAHs were detected and 11 had quantifiable concentrations.

The most dominant individual PAHs in terms of concentration were phenantrene (58%), benzo(g,h,i)perylene (31%), fluoranthene (3%), pyrene(2%), benzo(e)pyrene (2%) and benzo(a)pyrene (2%) in decreasing order.

The concentration of Σ13 PAH in all sediments was several folds lower than the TEC and PEC values proposed by Macdonald et al., suggesting no toxic effect on benthic organisms (Macdonald et al., 2000). Same conclusion can be drawn from the stricter sediment guidelines developed by Smith et al. (1996).



(a) PAHs (b) PCBs

Figure 12: Concentration of PAHs and PCBs [ng/g] in soil and sediment samples.

No clear trend exist between the PAHs concentration of the different sites and type of samples. The site presenting the highest PCBs (4.38 $\mu g/kg$) and PAHs (96.42 $\mu g/kg$) content is Tep1, situated in the Technopole Lake. Contamination of the two other sediments from the Technopole lake was remarkably lower with a PAHs concentration of 11.33 to 12.50 $\mu g/kg$ and the absence of PCBs (below detection limit). The higher content in Tep1 may be related to its high content of organic matter and smaller particle grain size (see section 3.1).

Senegal is part of the Stockholm convention about persistent organic pollutants (POPs) since 2003 and revised his National Implementation Plan in 2014. In keeping with the Stockholm convention, Senegal does not anymore produce neither uses the industrial chemicals PCBs. Despite this, uncontrolled uses have been observed in the agricultural sector, including in the market garden crops situated close to the Technopole lake (Pesticide Action Network, 2018). Actually, the southern hemisphere is expected to have a lower risk of PCBs contamination than the northern hemisphere since consumption of these compounds mainly occurred in the northern hemisphere (97% of global production). Nevertheless, leakage and wrongly disposed transformers, import of e-waste from countries of the North, shipwreck, biomass burning, uncontrolled burning of the chlorine-containing waste products (for instance PVC plastics) could be sources of PCBs. Therefore, an inventory of electrical transformers and capacitors associated with unintentional releases of PCBS was conducted in order to reduce them.

In this investigation, only the congeners 101, 138, 149, 153, 180 and 28 were detected from the 9 PCBs studied and only a few sites were contaminated (less than 30 % of samples). Indeed, sediment sample from Tep1 was the only site with a quantifiable concentration of total PCBs (Σ9PCB of 4.38 $\mu g/kg$). PCBs concentration were below detection limits for almost all other samples, except for PCB149 in soil sample Mb7 and PCB153 in sediment sample Mb3. Thus the PCBs levels in this investigation remained very low compared to ISQG (34.1 $\mu g/kg$) and PEL (277 $\mu g/kg$) value and will very likely cause no effect on sediment-dwelling organisms in freshwater ecosystems (Canadian Council of Ministers of the Environment, 2001). Same conclusion an be drawn by comparing with the sediment guidelines developed by Macdonald et al. (2000).

PCBs concentration in soil samples (<LOQ_{PCB}= 0.6 $\mu g/kg$) are also below soil quality guidelines of 33 $\mu g/kg$ for industrial soil but nothing can be said about the reference value of 0.5$\mu g/kg$ for agricultural soils (ibid.).

Although uncontrolled disposal of a high variety of waste and open burning for recovery of valuable metals are common practices in Mbeubeuss, almost no traces of PCBs were found. Soils and sediments samples were not collected directly on the discharge, but at a few hundred meters. Results could be explained by small travelling distances of these contaminants.

In this work, PAHs ratios were used to identify the origin of PAHs contamination. The sources of PAHs emission in the environment are mainly anthropogenic although natural sources such as forest fire exist. They can be divided in 4 important types: industrial sources (waste incineration, manufacturing of products such as metals, dye, coal-tar and pesticides, power production), mobile sources (exhaust from vehicles), domestic sources (garbage burning, wood burning, cooking on gas burner or with charcoal, etc.) and agricultural sources (open biomass burning) (Patel et al., 2020).

The LMW/HMW ratio gives information about their origin of production, i.e. whether the source is pyrogenic (lower than one) or petrogenic (higher than one). The results shown in Table 11 indicate that PAHs may be derived from petrogenic origins for most sites. Petrogenic PAHs include PAHs present in coal, coal tar, petroleum and various refinery products, which may end up in the environment due to unintentional leakages during storage, transport, use or disposal. Tep1, Mb9 and Mb3 presented ratios lower than one, suggesting pyrogenic origins of PAHs. Pyrogenic PAHs are unintentionally formed during incomplete combustion under low or no oxygen conditions of organic materials and through intentional pyrolytic processes.

Other common diagnostic ratios were used when possible (quantifiable concentration). The ratio BaA/(BaA+Chry) was between 0.2 and 0.35 in Tep1 and Mb7, meaning that the source was the combustion of coal, whereas both ratios Fluo/(Fuo+Pyr) and IDP/(IDP+BghiP) were lower than 0.2 pointing at a contribution from petrogenic source.

In brief, the results indicate that all samples contained rather petrogenic PAHs except Tep1, Mb3 and Mb7 where it may be a mix of pyrogenic and petrogenic origins.

Table 11: LMW/HMW PAHs ratios [%] for soil and sediment samples.

Sample	Mb1	Mb2	Mb3	Mb4	Mb5	Mb9	Tep1	Tep3	Tep4	Tep5.1	Tep 5.2
Type	soil	sed.	sed.	sed.	sed.	soil	sed.	sed.	sed.	soil	soil
LMW/HMW [%]	9.9	30.6	0.4	7.4	23.1	0.5	0.4	16.1	13.9	31.1	5.7

To our knowledge, no data about POPs in soils and sediment of the Technopole area were reported by another study. Regarding the landfill site, 7 PCBs congeners and 16 s were analysed in 2 zones called Gouy Gui, located east of point MB2, and Baol, situated at the east of the landfill, where its width is more important. PAHs and PCBs were detected in 4 soil samples (out of 6), with total concentrations ranging from 30 to 110 ng/g and from 3.4 to 16 ng/g respectively (LOQ$_{PAH}$=320 and LOQ$_{PCB}$=14) (Ministère de l'environnement et de la protection de la nature, 2011). Their results are in line with this study, although a few values are higher, probably due to a lower distance to the discharge. In addition to that, analysis of wastes gave concentrations up to 40 and 200 times higher in PAHs (130 to 2'180 ng/g) and PCBs (2.2 to 670 ng/g) (ibid.).

The Pesticide Action Network found high level of PCBs in eggs (1.7 times higher than EU limitations) coming from the surroundings of the landfill.

According to a study about POPs contamination in the sediments of coastal areas of Dakar, the mean pollution measured in sediment was 197 ± 240 $\mu g/kg$ (ranged from 1 to 636 $\mu g/kg$) for Σ16 PAHs and 58±81 (from 4 to 333) $\mu g/kg$ for Σ28PCBs (Net et al., 2014). The Mbeubeuss and Technopole mean concentrations of Σ10PCBs (0 ± 0 and 0.88 ± 1.96 $\mu g/kg$) and Σ14PAHs (28.7 ± 12.9 and 29.0 ± 37.7 $\mu g/kg$) measured in this work are lower. The sites chosen by their study are marine ecosystems located near important industrial sites in Dakar, which is not the case for the Technolople lake and Mbeubeuss landfill and they analysed a higher number of congeners.

PCBs and PAHs were also detected in seven selected marine species but in concentrations low enough to present good quality for human consumption based on the EU legislation. They did not determine the origin of the contamination but assumed it could be due to unintentionally atmospheric deposition, released from equipment, generators, ships, vehicles and trucks exhaust in the surrounding zone (ibid.).

M. Diop et al. found that most studied marine species from the Senegalese coast, including three sites located in Dakar, had PAHs and PCBs content below recommended EU value for human consumption. However, sardines from Rufisque (east suburb of Dakar) had PAHs content above the EU guideline. Moreover, their calculation of cancer risk (CR) for PAHs and PCBs at Soumbedioune and Rufisque showed an excess carcinogenic risk to the local population for most fish products, especially sardines *Sardinella*) and mussels (*P. Perna*).

Bodin, N'Gom Ka, et al. also observed significant levels of PCBs ranging from 0.3 to 19.1 $\mu g/kg$ in surface sediments, bivalves and gastropods from Falia (Sine-Saloum Estuary) and Fadiouth (Senegal) (Bodin, N'Gom Ka, et al., 2011). Moreover higher values were observed just after wet season in comparison with dry season. Results from the exposition of mangrove molluscs to contaminated sediment revealed no toxic effect and no potential risk for marine life and humans.

Air contamination in POPss was also evaluated in the context of the Stockholm convention, by monitoring a urban industrial site in Dakar. They found that it was one of the most polluted site from the the studied African countries with regard to PCBs, PAHs and DDTs (UN, 2009).

However, the values of POPs concentration in soil and sediments measured in Dakar during this investigation were lower than those recorded in numerous studies in Africa. Indeed, Quinn et al. found PAH concentration in areas of South Africa ranging from 0.1 to 6 700 ng/g with an average $\Sigma PAHs$ of 15 000 ng/g in soils and

670 ng/g in sediment (Quinn et al., 2009). A study conducted by Rimayi et al. revealed $\Sigma 31 PCBs$ ranging from 2.9 to 61 ng/g and average $\Sigma 16 PAH$ concentrations of 1 130 and 1 060 ng/g in the Klip and Jukskei River sediments (Rimayi et al., 2017). They mentioned that their concentrations were significantly lower than those recorded in big cities in China and India. Total concentrations of all PAHs measured (ΣPAH) were 260 to 14 000 ng/g in Kingtom (Sierra Leone) and 1 300 to 16 000 ng/g in Agbogbloshie (Ghana) samples, whereas PCBs concentration ranged from 0.74 to 43 ng/g in Kingtom, and from 6.5 to 830 ng/g in Agbogbloshie (Leung et al., 2015).
In Nigeria, studies were conducted in different environmental context and authors found the following average concentrations: $\Sigma PAHs$ of 119 and 18.5 ng/g in soil sample from mangrove forest respectively affected and not affected by fires, $\Sigma PAHs$ of 3 340 ng/g in landfill soil and $\Sigma PAHs$ 373 ng/g in urban soils (Olatunbosun S. Sojinu et al., 2011, Tongo et al., 2017, O.S. Samuel Sojinu et al., 2010).

Globally, soils and sediments from both sites appear unpolluted with regard to PAHs and PCBs concentration (Patel et al., 2020). Nevertheless, these highly persistent pollutants may increase in the next years and should be constantly monitored because of their high toxicity. Moreover samples collected at the discharge level may be too far away to assess its impact.

3.4 Tire related compounds

The tire additives concentration are given on the following Figure 13 as well as in the Appendix E, Tables 21 and 20. The results of the recoveries test of the solid phase extraction showed that some additive concentrations could be under- or overestimated. Therefore, it should be kept in mind that real concentrations may vary, by a factor of 0.9 to 2.3 according to the tests. Moreover, recoveries of ISTD of aniline and 6PPDQ were low and may lead to biased results (see Appendix F for more details).

Not all the additives studied are specific to tires. Indeed, benzothiazole derivatives (2-HBTH, BTH, 2-ABTH, SBTH and MTBT) are massively used in industrial and household applications mainly as vulcanization accelerators, corrosion inhibitors or biocides (but also for instance as anticancer agents or photosensitizers) (Herrero et al., 2014). The vulcanization accelerator CHA is also used as corrosive inhibitor or buffering agent in the synthesis of insecticides, plasticizers, emulsifying agents, dry-cleaning soaps and acid gas absorbents (Pubchem). The additive 6-PPD, an antioxidant and antiozonant, is added to rubber and polymers in order to extend the life of the product. It is mainly used in the rubber industry but also in the preparation of dyes, lubricants and house-hold products (Varshney et al., 2022). It can be transformed into 6-PPDQ, a compound known for its implication in salmon mortality (Kyoshiro et al., 2021). Finally, aniline, which is used as accelerator and anti-oxidant in rubber, is also employed in dyes and intermediates, photographic chemicals, in pharmaceuticals, explosives, petroleum refining and in production of diphenylamine, phenolics, herbicides and fungicides (NTI). Although tire derivatives have various applications, Kreider et al. found that individual concentration of DPG, 6-PPDQ, 2-ABTH, 2-HBTH and MTBT were correlated with styrene buadiene rubber and butadiene rubber in water samples they collected in an urban tributary, meaning that they may have common origins.

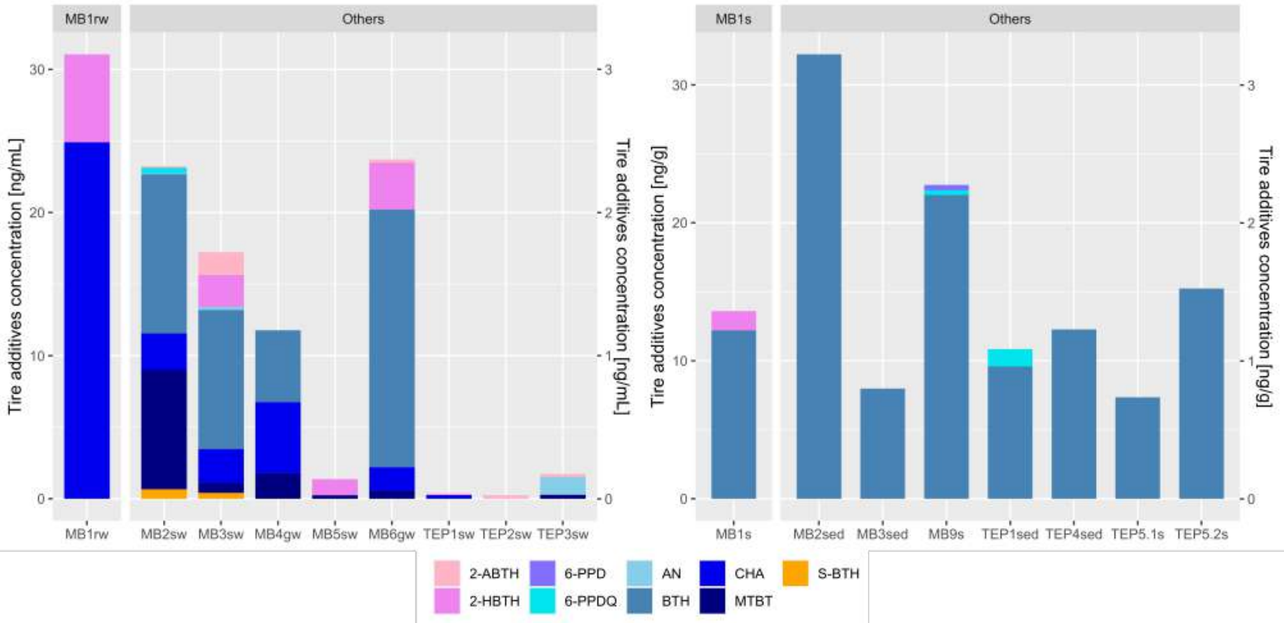


Figure 13: Tire additives concentration in water (left) and soil/sediment samples (right). Note that the y-axis scale is not the same for sampling point MB1 (factor of 10). No tire additives were detected in remaining samples (MB7sw, TEP4sw, MB5sed, MB7sed, TEP3sed).

3.4.1 Water samples

8 of the 10 substances analyzed were found in water and on average less than 3 compounds were detected in each sample, as can be seen in Figure 13 and Table 14. The total concentration of the studied substances in the water samples follows the order: MB1rw> MB6gw> MB2sw> MB3sw> MB4gw> TEP3sw> MB5sw> TEP1sw> TEP2sw> TEP4sw= MB7sw.

Table 12: Mean tire additives concentrations [ng/L] in water samples from Mbeubeuss landfill and Technopole (± standard deviation).

Tire additives mean concentration [ng/L]	Mbeubeuss [a]				Technopole	
	Superficial water		Groundwater		Superficial water	
	(n=4)	Std	(n=2)	Std	(n=4)	Std
AN	7,6	±11,2	0,0	±0,0	31	±62
CHA	123,3	±142,6	331	±235,4	6,5	±13
2-HBTH	83,6	±106,5	164,2	±232,2	0,0	±0,0
BTH	520,4	±603,6	1151,3	±918,5	0,0	±0,0
2-ABTH	43,1	±78	11,6	±16,4	14,6	±11,1
SBTH	26,6	±32,3	0,0	±0,0	0,0	±0,0
MTBT	231,7	±402,6	116,6	±87,3	6,7	±13,4
6PPD Q	9,6	±19,2	0,0	±0,0	0,0	±0,0
Σ_{10}additives	1045,8	±1157,1	1774,7	±844,4	58,8	±77,1

[a] *Sample Mb1 of rain water is not included in any mean due to its different nature.*

Sample MB1 (rainwater standing in a tire) had very high values for CHA and 2-HBTH, i.e. ten times above the other samples. Its total content, Σ_{10}additives of 31,05 ng/ml, is clearly above what can be found in environmental samples. Indeed, Rauert et al. found a maximum value of 2,76 ng/mL for 15additives in water collected

in the Brisbine river (Australia) during a major storm event, period of highest concentration due to important contribution of runoff water.
Other compounds were not detected in MB1 by direct injection and, unfortunately, no sample left was available for solid phase extraction, as in the case of TEP4, meaning higher quantification limits than in the other samples (see appendix F). Sample MB1 has been in contact with the tire for about 11 days (which is when the last rain event occurred) and therefore CHA and 2-HBTH very probably leached out from it, although they are not specific to tires.

Mean value in Technopole superficial water of 58,8 ± 77,1 (Σ_{10}additives) were similar to baseflow levels (i.e. in the absence of storm or with minor precipitation of 2mm) that were observed in the study of Rauert et al.: 63 ($\Sigma_8$additives) and 88 ng/L ($\Sigma_9$additives).
The mean amount of each tire additive present in superficial water was lower in the Technopole lake than at Mbeubeuss landfill, with the exception of aniline. Moreover, the mean Σ_{10}additives of 1'045,8 ± 1'157,1 was more than 10 times higher than that of the Technopole. Groundwater from Mbeubeuss still had greater values, with a mean Σ_{10}additives of 1'774,7 ± 844,4 due to a higher content of CHA, 2-HBTH and BTH, while aniline, 2-ABTH, SBTH, MTBT and 6PPDQ had a lower concentration than in superficial water.
The order of magnitudes observed at the Mbeubeuss landfill are 10 times above baseflow levels defined by Rauert et al., thus being closer to the level they observed during storm events for Σ_{15}additives (including 6PPDQ, benzothiazole and benzotraizole derivatives but also hexa(methoxymethyl)melamine (HMMM) derivatives and aromatic amines).

BTH has the highest concentrations, ranging from 502 to 1'801 ng/L in water samples from Mbeubeuss, which is similar to what they found in the Pearl River in China (30-1'082 ng/L)(Han et al., 2020). These concentration are far below the reported in vivo toxicity for aquatic organisms, i.e. below the lowest observed effect concentration (*LOEC*) and EC_{50}, which are above 680 000 ng/L according to Liao et al.).

Moreover, the measured concentrations for 2-ABTH, 2-OHBT, and 2-MTBT ranging from 12 to 835 ng/L were in line with the results of Rauert et al. (1,3 to 450 ng/L). Same order of magnitude were observed for 2-OHBT and 2-MTBT in studies from China, Germany and Spain (Varshney et al., 2022). These concentrations are also well below the *LOEC* and EC_{50} values reported by Liao et al. Finally, this is also the case for AN and CHA according to EU and Australian norms (AGI; UE)

Seasonal variations may have a big influence on additive concentrations. On one side Varshney et al. showed that tire additive concentration increased more than 40 times during storm events in the Brisbane river (Australia). On the other side, Han et al. observed a dilution effect (due to heavy rainfall and strong runoff) for benzothiazole and benzotriazole compounds, leading to lower additive concentrations (3-4 times) during the wet season in the Pearl River (China). As both phenomena could occur on the studied sites, it would be very interesting to compare data collected at the wet and dry season to be able to observe the influence of storm events on these additive concentrations.

The lower values observed at the Technopole site, situated right next to the most important roads of Dakar, leads to believe that tire wear particles from road traffic are not the only sources of additives. Wastes from the landfill such as rubber, polymers, dyes and pharmaceuticals, as well as phytosanitary products used in the market garden crops may play a role in the high values observed in the Mbeubeuss area.

Table 13: Range [ng/L] and detection frequency [% of tire additives concentrations in water samples from Mbeubeuss landfill and Technopole. *Sample Mb1 of rain water is not included in Mbeubeuss due to its different nature.*

Compounds	Range [ng/L][a]		Detection frequency [%]		
	Mbeubeuss	Technopole	Mbeubeuss	Technopole	Overall
AN	7-24	124-124	33	25	30
CHA	164-497	26-26	67	25	50
2-HBTH	112-328	0-0	50	0	30
BTH	502-1'801	0-0	67	0	40
2-ABTH	13-160	12-25	50	75	60
SBTH	41-66	0-0	33	0	20
MTBT	24-834	27-27	83	25	60
6PPD Q	38-38	0-0	17	0	10
6PPD	0-0	0-0	0	0	0
DPG	0-0	0-0	0	0	0
Σ_{10}additives	135-2'372	25-172	83	75	80

[a] Lowest value of the range is the minimum value above 0.

The absence of DPG can probably be explained by the high quantification limit achieved in this study (LOQ_{DPG}=389/ 2'090 ng/L, see Appendix F for more details). Indeed, DPG has been measured in surface water at level below or close to this value in Europe (up to 100 ng/L), in the USA (0,5540 ng/L) and in Australia (131079 ng/L) (Hou et al., 2019; Schulze et al., 2019; Varshney et al., 2022). 6-ppd was not detected either, but this substance is known for its rapid degradation in water (half-life of 6PPD of 8 h at 10 °C, according to Hiki et al.). This compound was not at all recovered from samples artificially spiked with derivatives (see Appendix F).

6-PPDQ has only been detected in a pond located 150 meter from Mbeubeuss (MB2sw), at a concentration of 38,4 ng/L. This is below the 24h LC_50 (concentration of a substance that will lead to the deaths of 50% of the population) estimates for coho salmon, that have been refined recently to 95 ng/L (Tian et al., 2022) and also below the LC_50 of 309 ng/L for zebrafish larvea (Varshney et al., 2022). Nevertheless, the measured concentration is of the same order of magnitude than LC_50 and could be higher during the wet season. Indeed, Varshney et al. compared tire additives concentration, including 6-PPDQ, during baseflow levels and storm events and highlighted a clear increasing trend. 6-PPDQ may have been released from TRWP or used rubber articles, dyes, lubricants and house-hold products coming from the landfill (ibid.).

3.4.2 Soil and sediment samples

The results of Pyr-GC-MS indicate that no pyrolysis marker was present in detectable amount in most soil and sediment samples (see Figure 28 Appendix E). The only chemicals detected were :

- Dipentene in Mb1 and Mb7
- Benzothiazole in Mb1 and Mb9
- TDQ and 2MT-BTH in Mb1

The LC-HRMS Orbitrap analysis of soil and sediment extracts allowed to quantify a few more compounds (BTH, 2H-BTH, 6-PPD, 6-PPDQ) with the following concentrations (details are given in Appendix E):

- Soil sample MB1

  $C_{2H-BTH} = 1,39 \pm 0,16\ ng/kg$
- Soil sample MB9

  $C_{6-PPD} = 0,03 \pm 0,00\ ng/kg$

  $C_{6-PPDQ} = 0,04 \pm 0,01\ ng/kg$

Table 14: Mean BTH concentration [ng/kg] in soil/sediment samples from Mbeubeuss landfill and Technopole (± standard deviation).

Tire additive mean concentration [ng/kg]	Mbeubeuss				Technopole			
	Sediment (n=4)	Std	Soil (n=2)	Std	Sediment (n=4)	Std	Soil (n=2)	Std
BTH	1,00	±1,52	7,20	±7,07	0,73	±0,64	1,13	±0,56

DPG and S-BTH/MBT were not detected in any sample and BTH, 2-HBTH, 6-PPD and 6-PPDQ were not identified in any other sample than those mentioned above.

The total concentration of the studied substances in the soil/sediment samples follows the order: MB1s> MB2sed> MB9s> TEP5.2s> TEP4sed> TEP1sed> MB3sed> TEP5.1s> TEP3sed= MB7sed =MB5sed.

Both methods detected the presence of benzothiazole in soil sample MB1 and MB9 but only the analysis by LC-HRMS gave BT concentrations for other samples, although some of them had a higher BT content than MB9. Reasons for that could be the inhomogeneity of samples and the different mechanisms of both analytical instruments (pyr-GC-MS is a destructive measure transforming the sample matrix into volatile gases, while LC-HRMS directly analyses the sample without previous transformation).

The presence of pyrolysis markers in the soil sample Mb1, especially the tread polymer dipentene, as well as 6-PPD and 6-PPDQ in sample MB9, suggest that tire dumping site can be a source of emissions of tire particles and/ or additives in the environment. This may be the case only over a very short distance, as samples are located less than 5 meters from the dumping sites.

The identification of BT, 2H-BTH and 2MT-BTH in the samples cannot undoubtedly be connected to tire wears, given that there are other sources of benzothiazole related compounds, as for instance antifreeze, which could either come from MSW or leak from automobile radiators (Baensch-Baltruschat et al., 2020).

The detection of dipentene in sediment Mb7 may be explained by the presence of a truck parking lot right next to the sampling point which generate truck traffic, a potential source of TRWP by abrasion of tires on the road. Given the very few results obtained from pyr-GC-MS, it goes without saying that no relationship between the distance to the road or to the dump and tire related compounds can be observed.

It is surprising that pyrolysis markers were detected in only three of the 11 samples analysed, while Panko et al. had a TRWP detection frequency of 97 % by measuring DP and 4-VCH in 69 roadside surface soils (0 to 15 meters from the road) and 149 sediments (at distances from the road varying between some meters and hundred of meters). The detection limit achieved in two of their studies was very low, ranging from 14 to 28 $\mu g_{TRWP}/g_{sample}$ (Panko et al., 2013; K. M. Unice et al., 2012). The technicians of the GR-CEL laboratory obtained higher detection limits. They were able to quantify tire particles in a natural soil artificially spiked with 5% CMTT, corresponding to approximately 25'000 $\mu g_{TRWP}/g_{sample}$ but not at 0.05 % CMTT (approx. 250 $\mu g_{TRWP}/g_{sample}$).

In a second step, the goal would have been to select reliable pyrolysis products such as DP and 4-VCH to quantify the total rubber concentration (NR+SBR+BR) in the sample and then deduce an approximate concentration of TRWPs. This was not possible given that most compounds were below quantification limits. The method used for the detection of tire related compounds should clearly be improved to obtain lower detection limits. Another solution would be to carry out a separation or concentration of tire particles to lower the sample matrix effects and increase the signal of pyrolysis markers. Methods that have already been developed for microplastics such as density separation followed by filtration or ASE could be tracks to explore (Picó et al., 2020).

Speltini et al. also analysed benzothiazole in soils collected in Northern Italy and obtained concentrations ranging from 611 to 786 ng/g in industrialized zones, whereas they did not detect any BTH in agricultural soils. Similar values were found in this study, except for the mean BTH concentration in soils collected at Mbeubeuss. This value is more than 7 times above, which suggests that BTH come from the tires stored nearby. The review of **liao** mentioned concentration ranging of 265 and of 50'000 ng/g in activated sludge from Germany and India, which should be more concentrated.

3.5 Non-target screening

The following figure shows the number of compounds detected in the samples, by site, as well as its reduction at each step of the selection process.

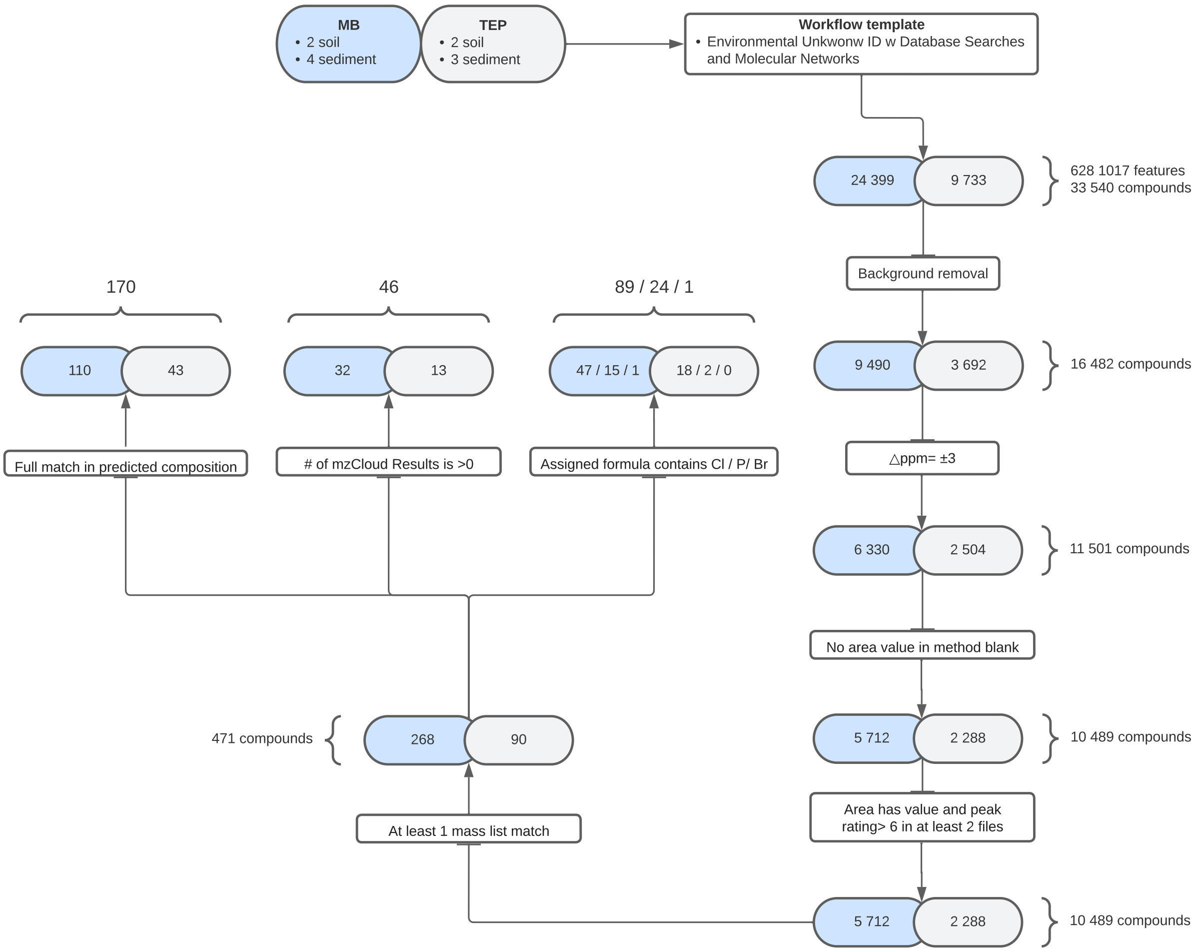


Figure 14

Because of the choice of workflow, without the post-processing nodes allowing to compare groups of samples, the filtering steps were carried out separately on three models: one with only Mbeubeuss samples, one with only Technopole samples and the last one with all samples. Therefore, the total number of compounds is not exactly equivalent to the sum of both sites, probably due to small variations of the model during the different runs. Ideally, the workflow should have been run again with the addition of post-processing nodes (differential analysis and descriptive statistics) but due to lack of time this was not done.

Among organochlorine compounds, the followings were identified and would deserve further analysis to confirm their presence :

Table 15: Results of the automatic identification of compounds in soil and sediment samples using Compound Discover. Only organochlorine compouds selected by the above mentioned filter and with confidence level above 5 are shown.

Tentative candidate	Formula	m/z	RT [min]	Application	Level of confidence	Sample
MCPB	$C_{11}H_{13}ClO_3$	227,04803	7,17	Herbicide	3	T5.2, MB3
Triclocarban	$C_{13}H_9Cl_3N_2O$	312,97082	8,86	Antibacterial chemical	3	T1, MB7
Cloprop	$C_9H_9ClO_3$	199,01674	8,14	Herbicide	3	MB7
Propiconazole	$C_{15}H_{17}Cl_2N_3O_2$	342,07703	8,41	Pesticide/herbicide	4	MB1

No MS2 spectrum were recorded for MCPB, Triclocarban and Cloprop, which could therefore not be compared with spectral libraries of experimental MS2 spectra or in silico predicted spectra. To increase the confidence of the tentatively identified compounds, the fist step would be thus to analyse again the samples to obtain MS2 fragmentation data. Their identity could eventually be confirmed by the analysis of a reference standard in order to reach a confidence level of 1.

The identification of propiconazole has been confirmed (level of confidence 1) thanks to the standards that were also analysed. Soil sample MB1, sediment MB3 and MB4 contain respectively 0.040 ± 0.020 ng/kg, 1.62 ±2.80 ng/kg, 3.07± 1.86 ng/kg. The presence of metoprolol, a beta blocker drug, was also quantified in the sediment TEP4, the soil TEP5.1 and TEP5.2 (the closest to the roads) and had the following concentrations: 1.23± 1.08 ng/kg, 8.43± 9.70ng/kg, 0.60± 1.04 ng/kg. All other compounds from the list given on Table 26 (appendix G) were below quantification limits. Most of these compounds were identified correctly by the Compound Discover software in the standards.

The whole raw list of substances kept after the filtering steps is given in appendix. More time is needed to analyse the data and select the relevant compounds to look for, as it has been done for organochlorine compounds.

3.6 Statistical analysis of data

3.6.1 Samples comparison

The results of the unsupervised clustering highlights the formation of four groups, according to the fusion level criteria (see Figure 15):

- Cluster n°1: MB1rw, MB6gw, MB7sw and MB9s
- Cluster n°2: TEP1sed and MB3sw
- Cluster n°3: Water samples from Technopole (TEP1sw, TEP2sw, TEP3sw, TEP4sw)
- Cluster n°4: Soil and sediment from Technopole and remaining samples from Mbeubeuss (MB1s, MB2sw/sed, MB3sw/sed, MB4gw, MB5sw/sed, MB7sw/sed)

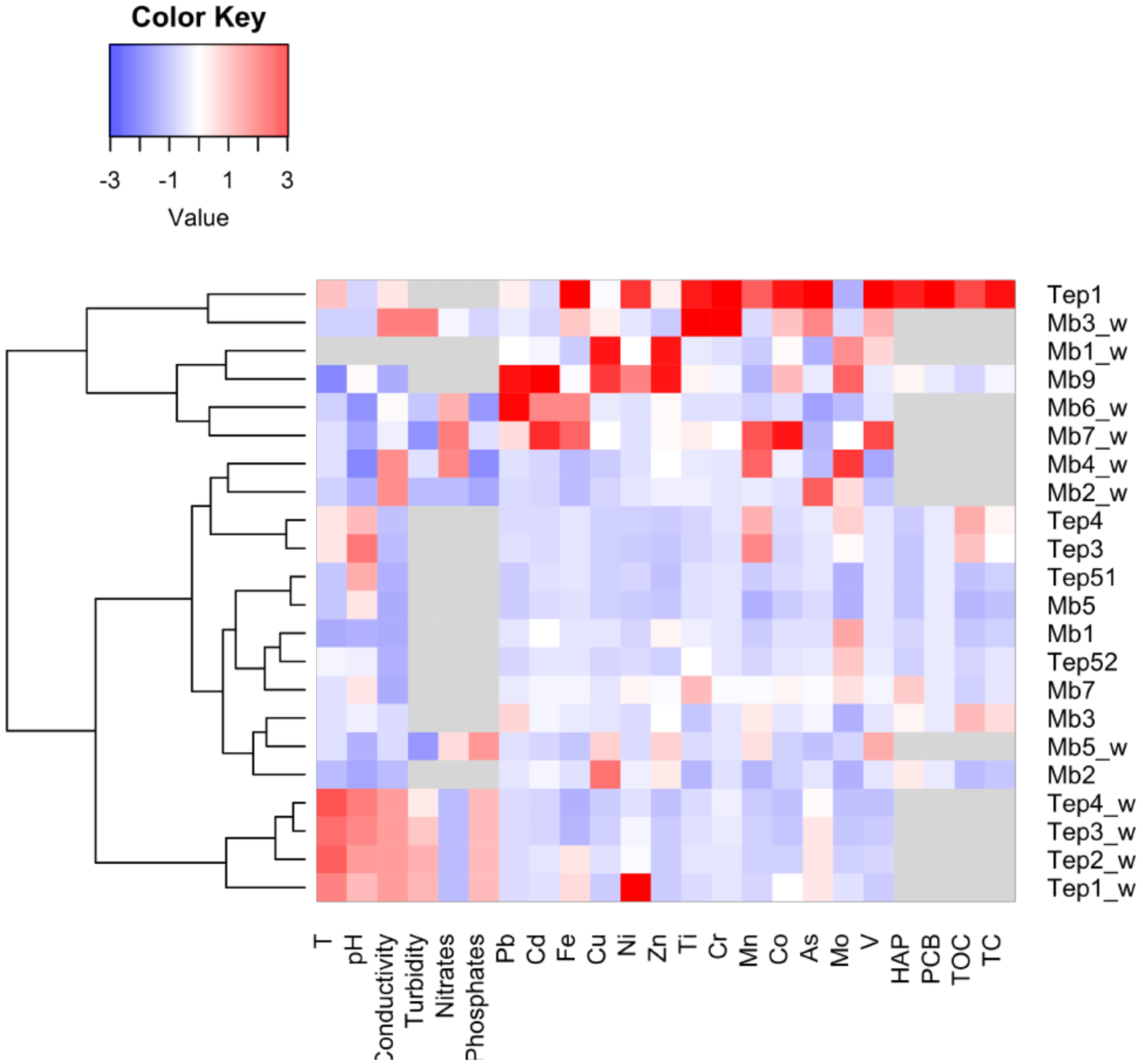


Figure 15: Heatmap of standardized data and dendogram obtained from hierarchical clustering of all available data. Heavy metal values were standardized separately, once in water samples and once in sediment/soil samples. Missing values are in grey.

As indicated by the dendogram, sediment TEP1 differs from the other samples of Technopole lake due to its high metal concentration (Ni, Cr, As, Fe, Ti, Mn, Co, V), high PAHs and PCBs content and high TOC/TC values. A very local discharge into the lake may be responsible for the pollution of the sediment sample Tep1. Although the point is the nearest to the WTTP of the Niaye, it is not likely to be the cause of pollution because the plant is located near the adjacent pond at a distance of about 900 meter, without any direct connection between both ponds. Further investigation is needed to identify the contamination source of this point, in order to take action in case of constant pollution of the urban natural reserve.

Apart from the sample Tep1, a few other samples stand out because of their high pollutant content, forming cluster n°1 and n°2 (see Figure 15) :

- Mb1 (rainwater) with high Ni,Cu, Zn, BTH, CHA
- Mb9 (soil) with high Pb, Cu, Zn, Cd
- Mb7 (surface water) with high nitrates and Cd
- Mb6 (surface water) with high Pb and Cd
- Mb3 (surface water) with high high Cr, As

The principal component analysis biplot on Figure 16 also highlights the contribution of Zn, Cu, Cd, and Pb to principal component 2 (PC2), which explains the formation of cluster n°1. It also confirms, by the position of Tep1 at the very right of the ordination plane, that it has very different features characterized by a high concentration of the metals whose arrow points to the right and rather low values for Cu, Cd, Pb, Mo and Zn.

Water from the Technopole lake has an overall better chemical quality, i.e. lower metal content, than samples from the landfill, with the exception of nickel and arsenic, as can be seen with the contribution of metals to PC1 and PC2 in Figure 42 (Appendix H). It therefore forms a separate cluster as can be observed on Figure 39 and 43 (Appendix H). Nevertheless, the PCA biplots with PC1/PC2 and PC3/PC4, the dendogram based on metals only and the metal heatmap (see H42,43 38) suggest that not only the metals contribute to the separation of Technopole and Mbeubeuss water samples in two clusters, but also the physicochemical parameters. Indeed, Technopole has higher values of temperature, pH, conductivity, turbidity and phosphates in Technopole, whereas Mbeubeuss has higher concentration of nitrates.

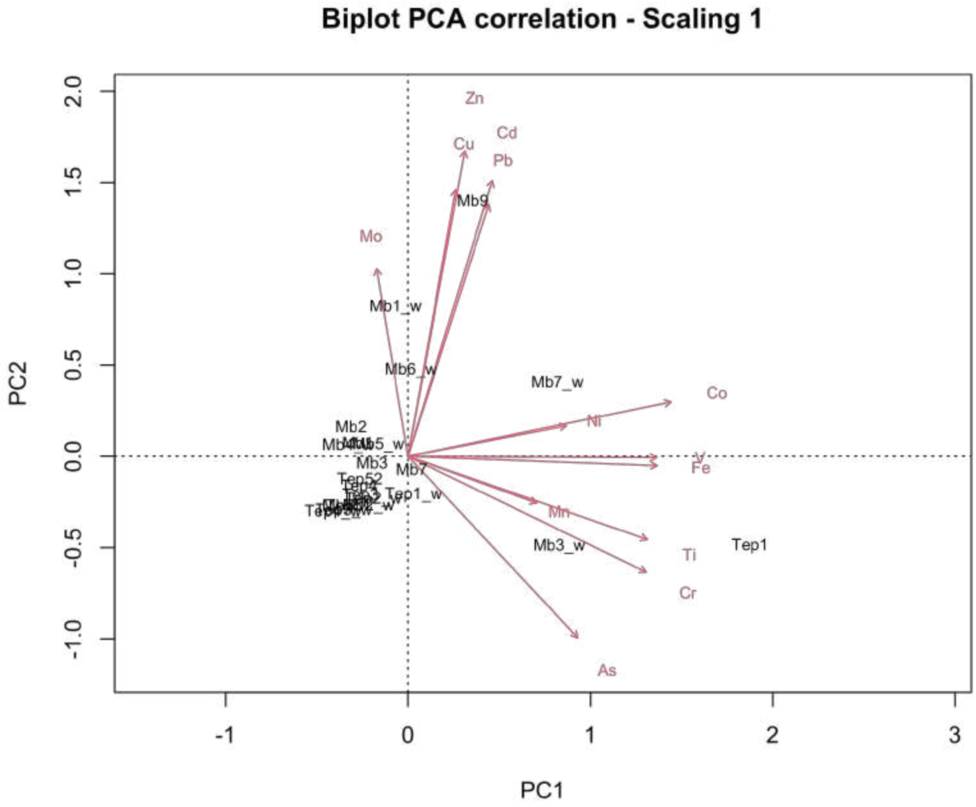


Figure 16: PCA biplot with PC1 and PC2 based on metal concentrations of soil, sediment and water samples. Principal components explain 37% (PC1) and 25% (PC2) of the metal data variance.

3.6.2 Relationships between variables

Metal correlation matrix

Figure 17 shows the Pearson correlations between heavy metals found in water, sediment and soil samples. In soils (n=4), most metals are highly positively correlated, except Mn which is negatively correlated with all metals. In sediments (n=7), the following metals have positive correlations (>0.9):

- Fe/ Ni/ Ti/ Cr/ Co/ As

The binding of heavy metals to the different components of the sediment matrix (organic matter, carbonates, charge minerals, organo-mineral complexes, microorganisms and phyllosilicates) is influenced by many parameters such as pH, nature and amount of components, concentration of ions and redox reactions. These sorption/desorption processes play a key role in the partitioning of heavy metal between sediment and water phases as well as in their bioavailability and potential toxicity for organisms.

Metal correlations in water (n=11) are much weaker than in soil and sediment (82% of values are between -0.5 and 0.5), the only correlations above 0.9 are:

- Cr/ Ti
- Cu/ Zn

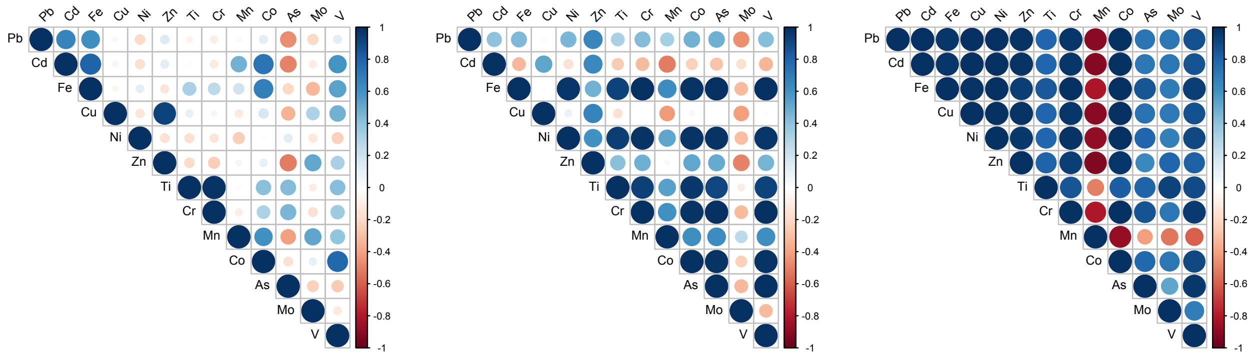


Figure 17: Correlation matrix between heavy metals in water, sediment and soil

4 Conclusion

In this project, samples from Mbeubeuss and Technopoles have been collected on site and analysed through different techniques. The conclusions of those analysis are summarised here.

Water samples from both sites do not meet the World Health Organization Guidelines Values for Drinking Water due to high heavy metal concentrations. Therefore, they should not be consumed by the population without prior treatment (WHO, 2017). Indeed, groundwater from Mbeubeuss, the drinking water resources of two third of the neighbouring inhabitants, exceed lead and cadmium GVDW. Superficial water coming from the lake of Mbeubeuss and from 3 ponds close to the landfill is of poor quality due to its arsenic and cadmium concentration, whereas the lake of Technopole has nickel values above the GVDW .
Moreover, the Environmental Quality Standards defined by the European Union with the aim of preserving ecosystems and avoiding health risks for humans are not respected either, due to the high nickel and cadmium concentrations in the Technopole lake and the high cadmium content of the superficial water of Mbeubeuss (EU, 2013). Eventually, arsenic concentration is above the Environmental Guide Values, derived by the National Institute for the Industrial Environment and Risks, in every superficial water sample (INERIS, 2015).

The calculation of enrichment factors showed that soil and sediment samples at the landfill level were severe to extremely severe enriched in Pb, Cd, Cu, Zn and As due to anthropogenic activities, while this was the case only for Cd at the Technopole site.
Less than 30% of the sediment samples had metal concentration above levels that are likely to be associated with adverse biological effects for benthic organisms (Macdonald et al., 2000). Two sediment samples, the first being in a pond situated at 150 m from the discharge, and the second in the lake of Technopole at 1.2 km from the highway, exceed sediment quality guidelines due to a high content of respectively Cu, and Ni, Cr and As.
The heavy metal contamination of sediment situated at more than 100 meters from the landfill seems to be little to not influenced by the latter, although high amounts of metal components are dumped on the site each year (2% of the total waste in 2020 PAGE, 2021). The lack of data does not allow to say anything about its effect at smaller distances. This confirms what was observed by Niang et al., i.e. that the influence of the landfill on heavy metal contamination is important only within a 50 meter radius.

Regarding soil quality, one of the two soil samples of Mbeubeuss, located at the landfill near a tire storage area, had Pb, Cd and Zn concentrations above the guide values of the Swiss legislation (Osol, 1998), meaning that its fertility is no longer guaranteed. Niang et al. pointed out that informal settlements are getting closer and closer to this area of the landfill, where soil inhalation or ingestion may present health risk for human and animal. Metal concentration in the second sample of Mbeubeuss as well as in the soil samples located near the highway of Technopole met the quality criteria mentioned just above.

The concentrations of polycyclic aromatic hydrocarbon and polychlorinated biphenyl in all sediments were several folds lower than the guidelines values proposed by Macdonald et al. and Smith et al., suggesting no toxic effect on sediment-dwelling organisms. All the tested sediments and soils presented detectable amount of PAHs, with Σ14 PAH ranging from 10.41 µg/kg to 96.42 µg/k, while only sample TEP1 had measurable PCBs content (i.e. Σ9 PCBs of 4.38 µg/k).

The calculated PAHs ratios indicate that most samples contained rather petrogenic PAHs, i.e. PAHs present in coal, coal tar, petroleum and various refinery products. In one sediment sample of Technopole and Mbeubeuss lake (Tep1, Mb3) as well as in the waterway south of the landfill, it is rather a mix of petrogenic and pyrogenic origins. Potential sources of pyrogenic PAHs, which are formed through incomplete combustion, could be diverse on both sites: industrial (waste incineration, manufacturing of products such as metals, dye, coal-tar and pesticides, power production), mobile sources (exhaust from vehicles), domestic sources (garbage burning, wood burning, cooking on gas burner or with charcoal, etc.) and agricultural sources (open biomass burning).

The values of POPs concentration in soil and sediments measured in Dakar during this investigation were lower than those recorded in coastal areas of Dakar and in numerous studies in Africa (Bodin, N'Gom Ka, et al., 2011; Net et al., 2014; Quinn et al., 2009; Rimayi et al., 2017). The evaluation of air contamination in African countries found that Dakar had one of the most polluted industrial site with regard to PCBs, PAHs and DDTs (UN, 2009). Although both sites appear unpolluted with regard to PAHs and PCBs concentration, the accumulation of these highly persistent pollutant in soil and sediment may increase in the next years and should be constantly monitored because of their high toxicity. Moreover, samples collected in the discharge area may be too far away to assess its impact. Indeed, much higher concentrations were found in soils and wastes located at shorter distances (Ministère de l'urbanisme, du logement et de l'hygiène publique et al., 2019).

Tire additives, including 5 benzothiazoles derivatives, DPG, AN, CHA, 6-PPD and its subproduct 6-PPDQ, as well as synthetic rubber, were analysed in water, soil and sediment samples. At least one substance was detected in 80 % of the water samples and in 70 % of the soil and sediment samples. Besides being used in tires manufacturing, most of these compounds have other applications mainly as corrosion inhibitors and antioxidants (Liao et al., 2018). The most abundant compound, in term of detection frequency and/ or concentration in water, soils and sediment was benzothiazole.

Both soils from tire storage sites MB1 and MB9 contained either a significant number of compounds and/or in proportions higher than the average concentration. The presence of pyrolysis markers in the soil sample Mb1, especially the tread polymer dipentene, as well as 6-PPD and 6-PPDQ in sample MB9, suggest that tire dumping site can be a source of emissions of tire compounds in the environment. This may be the case only over a very short distance, as these samples were located less than 5 meters from the dumping sites.

Tire additive concentrations in superficial water were lower in the Technopole lake than in the ponds and lake situated near the Mbeubeuss landfill. The mean value in Technopole superficial water of 58,8 ± 77,1 (Σ_{10}additives) was similar to the baseflow levels (i.e. dry weather) observed in the study of Rauert et al. The average order of magnitude of these compounds were 10 times higher in groundwater and superficial water at the Mbeubeuss landfill. These values, with a mean Σ_{10}additives of 1'289 ± 1043, are in line with previous

published data for additive in superficial water.
The main roads of the city being in the Technopole site area, where lower concentrations were found, suggests that tire additives may have additional sources of emission, such as wastes from the landfill (rubber, polymers, dye, pharmaceuticals, etc) and phytosanitary products used in the market garden crops. At the technopole site, no trend in the tire related compounds was observed by increasing the distance to the road (0 to 1170 meters).

6-PPDQ, an acutely toxic substance responsible of mass death coho salmon, has only been detected in a pond located 150 meter from Mbeubeuss (MB2sw), at a concentration of 38,4 ng/L. This is below the 24h LC_{50} estimates for coho salmon of 95 ng/L (Tian et al., 2022). Nevertheless, this toxic additive should be monitored, especially during wet season, where its value may increase due to stormwater. 6-PPDQ may have been released from TRWP or used rubber articles, dyes, lubricants and house-hold products coming from the landfill (Varshney et al., 2022).
All other additives were far below the toxic levels of various aquatic organisms ($LCOE$ and EC_{50}) (Liao et al., 2018).
Seasonal variations may lead to an increase or decrease in additive concentrations, depending on the relative importance of the dilution effect and the transport of pollutants caused by runoff water and rainfall (Han et al., 2020; Varshney et al., 2022). Therefore, it would be very interesting to compare data collected at the wet and dry season to be able to observe the influence of storm events on the additive concentrations at Mbeubeuss and Technopole sites.

The comparison between Mbeubeuss and the control site (Technopole) reveals that both sites are actually affected by urban pressure, showing anthropogenic pollution. Although most contaminants analysed showed lower values in the area of the Urban Reserve, one sampling point north east of the lake showed especially high contamination. Further investigation is needed to determine the causes and sources of pollutants' emission, in order to put in place measures for the preservation of the Urban Nature Reserve.

The few water and sediment samples collected at the discharge level, at distances ranging from 60 to 420 m, were not sufficient to determine the impact of the landfill on the surrounding environment. Other sources, such as the bad sanitation system and the use of pesticides in garden market crops may play a more important role on the observed contamination at these distances. Nevertheless, the risk posed by the landfill for the neighbouring populations and the environment is no longer to be proven and the rehabilitation project of the site must absolutely be carried out. Moreover, a solution must be found to substitute the source of drinking water for the populations, which present a bad microbiological and chemical quality.

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Appendices

A Sampling campaign

(a) MB1 (b) MB2

(c) MB3 (d) MB7

Figure 18: Sampling sites in the landfill of Mbeubeuss

(a) TEP1 (b) General context

(c) General context (d) Boat used for sampling

Figure 19: Urban Nature Reserve of the Grande Niaye of Pikine

B Heavy metal concentrations

B.1 Water, soil and sediment samples

Table 16: Heavy metal concentration [$\mu g/l$] in rainwater (rw), superficial water (sw) and groundwater (gw) at Mbeubeuss and Technopole sites.

Heavy metal concentration [$\mu g/l$]	Mbeubeuss							Technopole				WHO quality guidelines[a]	MAC-EQS/ VGE[b]
	MB1 rw	MB2 sw	MB3 sw	MB4 gw	M5 sw	MB6 gw	MB7 sw	TEP1 sw	TEP2 sw	TEP3 sw	TEP4 sw		
Pb	5,00	0,13	2,46	0,90	0,88	36,4	9,69	0,04	0,41	0,28	0,12	10	14
Cd	0,83	0,07	0,07	0,11	0,12	3,92	6,14	0,27	0,47	0,05	0,07	3	0,45[c]
Fe	78,2	49,8	253	51,8	69,6	345	397	216	206	45,7	35,7		
Cu	16,5	1,43	4,84	0,89	6,36	2,66	4,03	1,02	2,13	1,07	0,91	2000	
Ni	77,0	29,6	28,2	17,2	11,1	22,6	18,9	556	65,8	63,1	20,4	70	34
Zn	260	45,9	14,1	63,4	106	67,7	68,3	18,0	17,7	14,6	7,03	(3000)[d]	
Ti	1,48	1,63	17,5	1,22	0,42	0,74	3,82	0,45	1,06	0,72	0,56		
V	5,70	1,93	7,07	0,66	7,36	3,10	11,1	2,07	2,54	1,97	1,71		
Cr	2,45	2,90	39,78	3,23	3,10	2,27	6,24	2,83	2,85	3,68	4,63	50	
Mn	61,1	229	144	1300	563	87,6	1410	109	85,9	86,5	68,6		
Co	1,58	0,78	2,64	1,06	0,50	0,83	5,80	1,48	0,48	0,31	0,21		
As	1,60	15,84	13,32	2,17	2,51	0,69	1,87	7,99	7,95	7,93	6,53	10	1,37
Mo	11,61	7,23	3,01	16,38	2,82	1,30	5,28	3,17	2,50	1,90	1,68		

[a] *Cells colored in red means an overcoming of WHO guidelines for safe drinking water (WHO, 2017).*

[b] *Values in red are above the Environmental Quality Standards (EQS) defined by the European Union (EU, 2013), except for arsenic which is compared to the Environmental Guide Values (EGV) derived by the National Institute for the Industrial Environment and Risks (INERIS, 2015).*

[c] *MAC-EQS of cadmium ranges from 0,45 to 1,5 $\mu g/l$ depending on water hardness. The lowest value was selected here as no indication about water hardness is available.*

[d] *There is no guideline value for Zn because it is not of health concern at levels found in drinking-water. Neverthless, WHO mentioned that "drinking-water containing zinc at levels above 3 mg/l may not be acceptable to consumers".*

Table 17: Heavy metal concentration [mg/kg] in soil (s) and sediment (sed) at Mbeubeuss and Technopole sites. Cells colored in pink means an overcoming of Probable effect level (PEL) and values in yellow are above Threshold effect level (TEL) proposed by Macdonald et al.

Heavy metal concentration [mg/kg]	Technopole				Mbeubeuss							TEC[a]	PEC[b]	ISQG[c]	PEL [c]	OSol [a]
	TEP1	TEP3	TEP4	TEP5.1	TEP5.2	MB1	MB2	MB3	MB9	MB5	MB7					
	sed	sed	sed	s	s	s	sed	sed	s	sed	sed					
Pb	18,2	5,9	4,7	1,6	3,5	8,0	8,0	24,7	69,7	2,0	8,2	35,8	128	35	91,3	50
Cd	0,0	0,0	0,0	0,1	0,1	0,2	0,2	0,2	1,7	0,0	0,2	0,99	4,98	0,6	3,5	0,8
Fe	64983	1692	2243	1719	2496	1644	1295	2961	6689	993	5430					
Cu	15,3	1,1	2,1	1,0	2,7	8,2	70,3	7,8	90,0	1,8	8,1	31,6	149	35,7	197	40
Ni	23,4	1,0	1,4	1,9	2,5	2,0	4,0	2,5	16,5	1,2	6,7	22,7	48,6			50
Zn	60,3	8,3	11,5	4,7	13,3	54,8	62,9	48,5	202,0	8,1	42,5	121	459	123	315	150
Ti	566,0	120,4	120,9	134,6	186,0	167,7	72,1	96,9	215,6	136,9	305,6					
Cr	207,6	3,3	4,3	5,2	7,4	5,3	3,7	7,2	17,6	4,5	19,9	43,4	111	37,3	90	50
Mn	153,0	128,5	103,7	28,9	35,2	27,9	15,9	73,4	17,5	13,1	54,0					
Co	5,6	0,5	0,6	0,6	0,8	0,7	0,4	0,8	2,5	0,3	1,6					
As	11,3	0,5	0,7	0,5	0,7	0,4	0,7	1,1	0,8	0,2	1,3	9,79	33	5,9	17	
Mo	0,0	0,3	0,4	0,0	0,4	0,5	0,0	0,0	0,7	0,0	0,3					5

[a] *Cells colored in yellow means an overcoming of TEC defined by Macdonald et al. or of the indicative value for soils defined by the Swiss legislation (Osol 1998)*

[b] *Cells colored in red means an overcoming of PEC defined by Macdonald et al.*

[c] *Interim freshwater sediment quality guidelines (ISQGs; dry weight) and probable effect levels (PELs; dry weight) from Canadian Council of Ministers of the Environment, 2001*

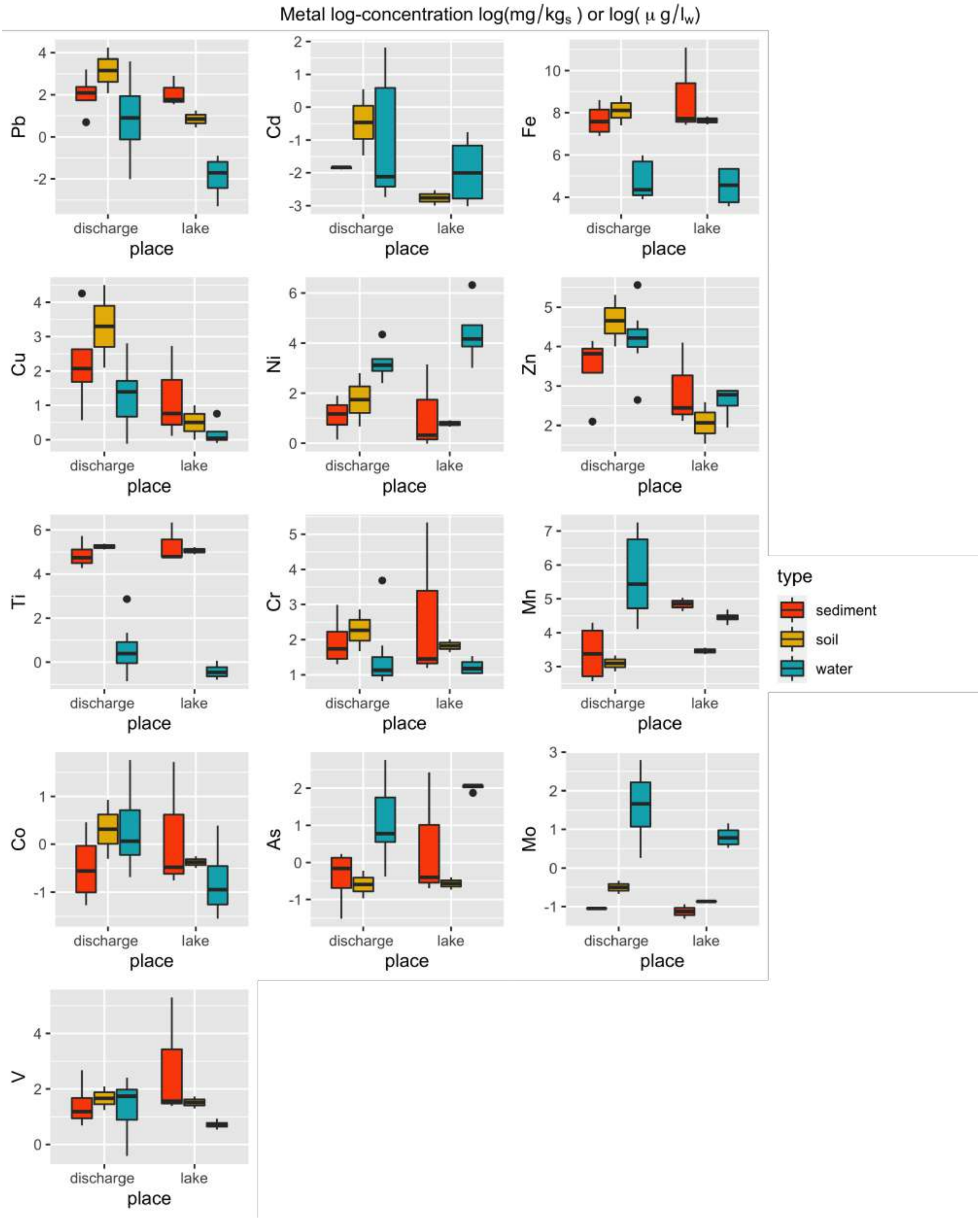


Figure 20: Heavy metals boxplot

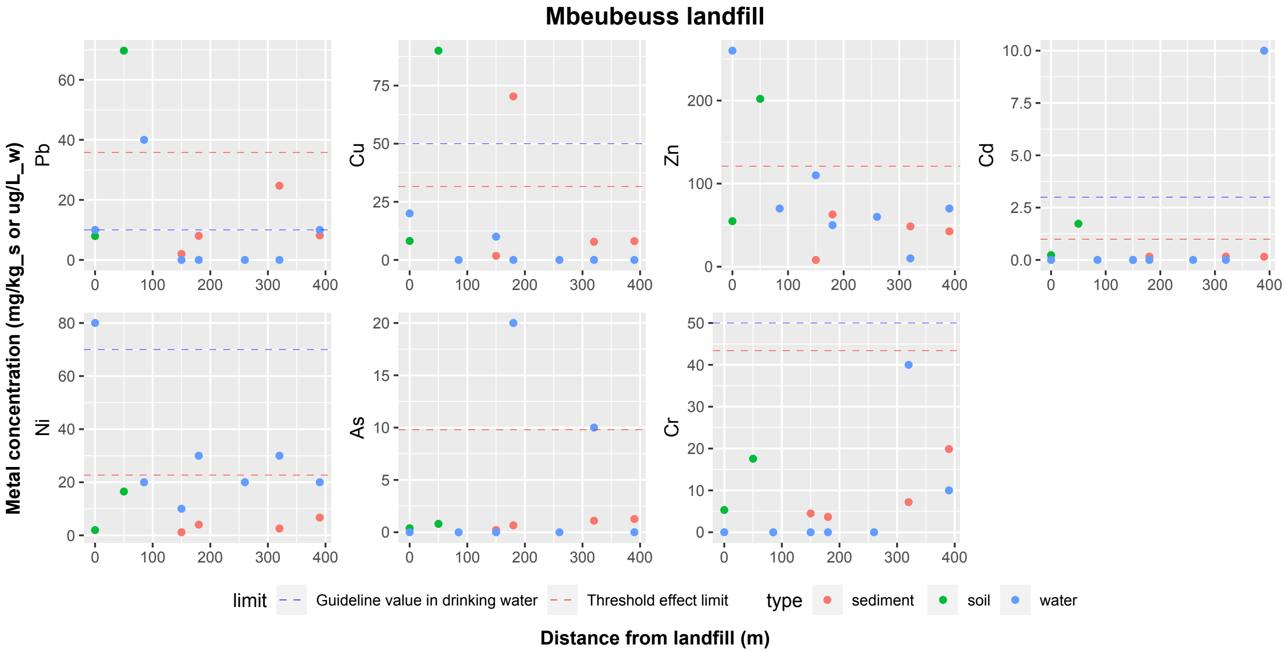


Figure 21: Heavy metal concentration as a function of the distance to the landfill.

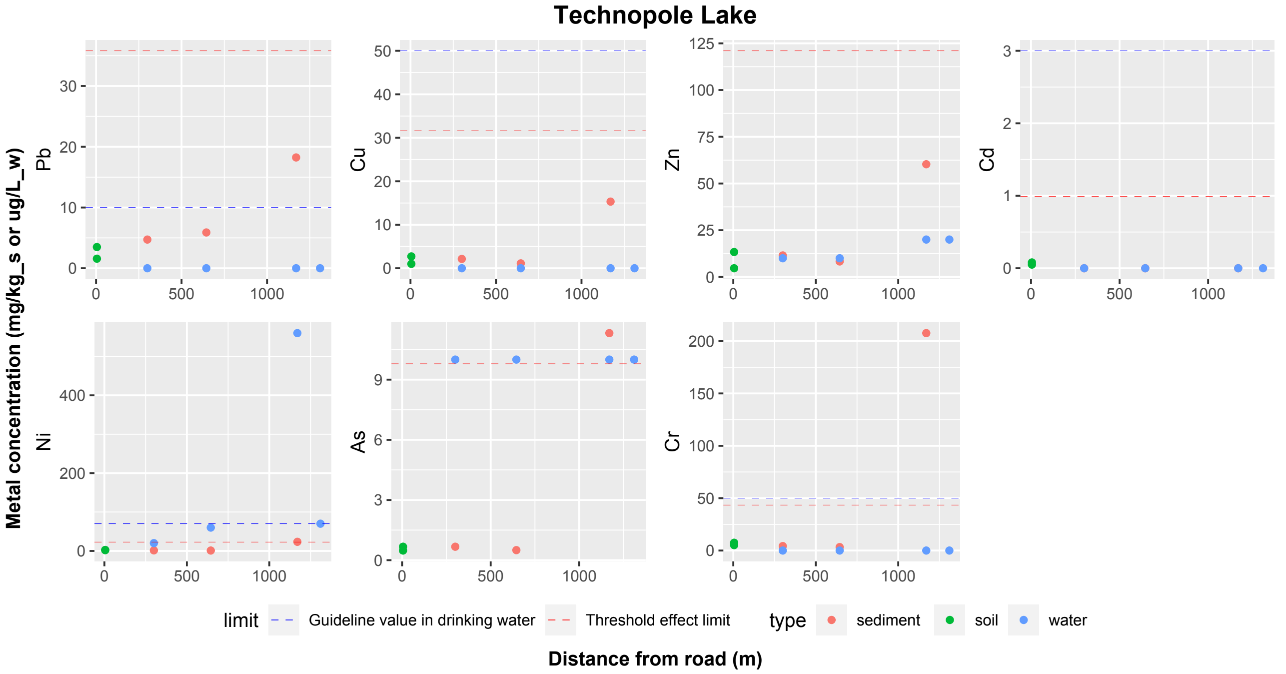


Figure 22: Heavy metal concentration as a function of the distance to the high road of Technopole.

B.2 Comparison between heavy metals in tire samples, CMTT, TRWP and RP

One of the initial goal of this project was to quantify TRWP in soil and sediment samples by pyr-GC-MS analysis. To this end, it was planned to make an external calibration by spiking tire particles in a natural soil. Ideally, the tire particles used should represent as good as possible the particles susceptible to contaminate the environment. In the case of Technopole and Mbeubeuss, they would consist of tire-road wear particles and possibly tire particles coming from the erosion of tires stored in the dumping sites (by water, wind or microorganisms). As these particles are not easily collectable, CMTT would have been employed as the best substitute for natural TP and TRWP. A conversion factor would have been used to estimate the TRWP equivalent which contain high amounts of mineral encrustations. In order to assess the consistency of this hypothesis, heavy metal concentration was measured in 4 tires coming from the Mbeubeuss landfill. Figure 23 and 24 show the heavy metal concentration in these tire samples and in cryogenically milled tire tread (CMTT), tire road wear particles (TRWP) and road particles (RP) data from Masset et al., 2021.

Sample **Concentration [mg/kg]**	**MB1** **(n=3)**	**sd**	**MB8** **(n=3)**	**sd**	**MB9** **(n=3)**	**sd**	**MB10** **(n=3)**	**sd**	**PS** **(n=3)**	**sd**
Zinc	7 404,8	0,4	18 107,9	716,0	9 292,8	165,6	9 465,3	571,0	122,57	5,47
Titane	28,3	2,2	57,6	3,8	18,1	1,4	14,1	1,9	1,97	1,32
Vanadium	0,9	0,1	1,8	0,1	0,7	0,0	0,7	0,0	<0,02	-
Chrome	6,0	0,3	11,7	0,3	10,2	0,2	5,4	0,1	0,82	0,35
Manganese	2,7	0,1	7,9	0,3	3,0	0,1	3,5	1,5	0,11	0,04
Iron	232,2	30,5	807,0	13,0	288,0	10,7	370,8	266,3	5,88	5,36
Cobalt	0,1	0,0	0,4	0,0	0,6	0,1	0,2	0,0	0,01	0,02
Nickel	0,7	0,1	6,5	0,3	1,9	0,1	2,0	0,0	0,08	0,15
Copper	11,7	6,5	18,0	0,4	5,7	1,0	3,1	0,1	<1,00	-

Figure 23: Metal concentration $[mg/kg]$ in tires collected in the Mbeubeuss landfill and in the polystyrene control *(sd=standard deviation, n=number of replicates).*

Sample **Concentration [mg/kg]**	**MB** **(n=12)**	**sd**	**CMTT** **(n=3)**	**sd**	**TRWP** **(n=3)**	**sd**	**RP** **(n=1)**
Zinc	11 067,7	4 350,0	7 780,0	69,0	1 448,0	76,0	<250
Titane	29,5	17,9	16,7	0,2	8,1	5,5	2,0
Vanadium	1,0	0,5	1,2	4,6	14,5	0,4	7,0
Chrome	8,3	2,8	4,9	0,5	229,0	36,5	30,8
Manganese	4,3	2,3	1,3	0,1	156,0	9,1	39,4
Iron	424,5	262,6	82,9	3,7	4 863,0	43,0	1 219,0
Cobalt	0,3	0,2	7,5	0,1	26,4	2,2	0,7
Nickel	2,8	2,3	3,3	0,2	26,0	2,4	2,8
Copper	9,6	6,6	2,3	2,3	53,3	20,9	2,5

Figure 24: Metal concentration $[mg/kg]$ in cryogenically milled tire tread (CMTT), in tire road wear particles (TRWP) and in road particles from Masset et al., 2021 *(sd=standard deviation, n=number of replicates).*

Tires sample MB1, MB9 and MB10 came from two dumping sites (sample MB1 from site MB1 and samples MB9 and MB10 from site MB9 on Figure 4) and sample MB8 comes from an isolated tire abandoned on the landfill (see picture in Figure25). Unfortunately, no background information is available about tire brands, their state of wear and tear or their storage time on the landfill. Nevertheless, it was deduced by observing and cutting the rubber that the state of wear of tires is likely to follow the order: MB1< MB8< MB9< MB10 (Mb1 being the least used tire). The composition of Mb samples is expected to differ from the composition of CMTT due to aging of the upper layer of tires through environmental processes such as thermooxidation, photooxidation, ozonolysis, shear stress, biodegradation and leaching (Wagner, Klöckner, et al., 2022). CMTT is a mix of three types of virgin tires cryogenically milled, therefore their composition should not change from the initial material.

(a) Tire samples MB1

(b) Tire sample MB9 and MB10

Figure 25: Tire dumping sites in Mbeubeuss landfill, where tire samples were collected.

Tire samples were ground with a grinding jar and balls made of stainless steel which contains manganese, chromium, nickel and iron. Retsh conducted metal contamination tests by grinding limestone with different grinding instruments made of stainless steel. They observed, as expected, a contamination in chromium, nickel and iron of respectively <1ppm to 26 ppm, <1ppm and 0.15 % (Retsh, 2013). Therefore, a control was carried out with polystyrene (PS) to evaluate the metal contamination during the grinding step of tires sample. Metal content of milled polystyrene is low in comparison with tires, representing less than <10% of tires' metal content and with a great variability between triplicates. Possible contamination related to the grinding step of tire samples is thus negligible. Therefore, no other tests were conducted to determine whether measured metal concentrations came from the grinding step or the polystyrene itself.

Metal concentration are below 60 mg/kg for each MB sample, except for Zn (11'068 ± 4'350 mg/kg) and Fe (424.5 ± 262.6 mg/kg). Tire sample MB8 has higher metal concentration than other MB samples and CMTT, apart from cobalt concentration. This may be explained by the time of storage on the landfill. MB1, MB9 and MB10 were found on tire dumping sites (see Figure 25) since a long time according to a recuperator of the landfill, whereas MB8 was simply left behind in a random manner, probably a short time ago. Thus, mineral material stemming from the road surface that might be encrustred on the upper layer of tires would have less time to leach out from MB8 than from MB1, MB9 and MB10, resulting in higher metal concentration.

Metal content of MB tire samples are very similar to CMTT. Ti, Cr, Mn and Cu are slightly higher than CMTT whereas Ni, Co and V are slightly lower. One hypothesis for the higher Fe, Cr and Mn content could be the incorporation of road particles and dust on the upper part of the tire treads, thus increasing their concentration and making the composition of tire particles more similar to TRWP. Lower content of Ni and Co may be also explained by the encrustment of road particles, which could lower the concentration of these metals by a dilution effect. Moreover, initial differences in tire composition between brands could explain the variations in heavy metals' concentration.

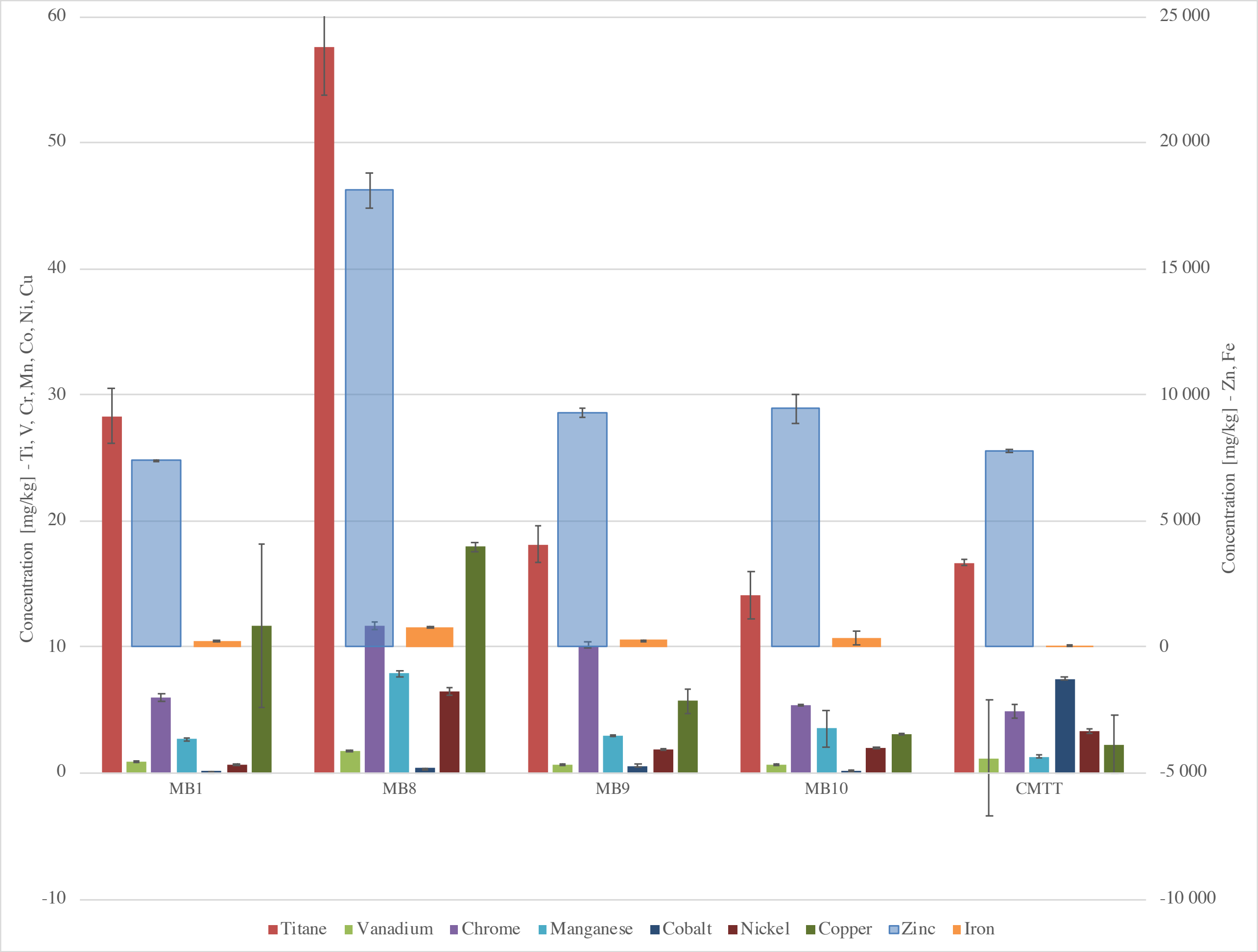


Figure 26: Metal concentration $[mg/kg]$ in tires collected in the Mbeubeuss landfill and in CMTT.

In brief, heavy metal composition of tire samples from the discharge very slightly differ from CMTT. This could be partly due to the aging of MB samples through environmental processes and/or initial variations in tires' composition.

C Details regarding the metal analyses with ICP-MS/MS and ICP-OES

C.1 Analyses of samples on ICP-OES

The plasma gas flow, auxiliary gas flow, carrier gas flow and nebulizer sample flow were 10 $Lmin^{-1}$, 0.6 $Lmin^{-1}$, 0.7 $Lmin^{-1}$ and 0.35 $mLmin^{-1}$ respectively. The samples were introduced into the cyclonic chamber with a MicroMist nebulizer (Agilent®) along with an internal standard of 10 ppm of Y. Calibration curves were calculated from 7 calibration points ranging from 0.05 to 20 mgL^{-1} of a multi-elements solution. Quality control samples (mgL^{-1}) of multi-elements solution (Inorganic Ventures®) were processed after each series of 10 samples.

C.2 Analyses of samples on ICP-MS/MS

The plasma gas flow, nebulizer gas flow (Argon)and nebulizer sample flow were 15 $Lmin^{-1}$, 1.07 $Lmin^{-1}$ and 0.35 $mLmin^{-1}$ respectively. The samples were introduced into the nebulizer chamber (MicroMist nebulizer Agilent®) with an internal standard of 1ppm of Sc, Y and Bi that was used for correction of matrix effects. Quality control samples were processed after each series of 10 samples and were composed of three concentrations (0.1, 1, 10 μgL^{-1}) of multi-elements solution (Inorganic Ventures®). When variability of quality control samples exceeded 10 %, results of the all batch were disregarded and a new batch was analysed. Calibration curves were calculated from 5 to 10 calibration points ranging from 0.01 to 50 μgL^{-1} of a multi-elements solution. Limits of quantification for the metals analysed ranged from 0.01 to 1 $\mu g/l$ in water samples and from 5 to 2500 $\mu g/kg$ in soil and sediment samples.

C.3 Details about limits of quantification, dilution and instrument used for each sample

Conc [mg/l]	MB1	MB2	MB3	MB4	MB5	MB6	MB7	TEP1	TEP2	TEP3	TEP4	LOQ
Pb	0,00500	0,00013	0,00246	0,00090	0,00088	0,03636	0,00969	0,00004	0,00041	0,00028	0,00012	0,00001
Cd	0,00083	0,00007	0,00007	0,00011	0,00012	0,00392	0,00614	0,00027	0,00047	0,00005	0,00007	0,00001
Fe	0,07824	0,04980	0,25264	0,05183	0,06957	0,34500	0,39654	0,21594	0,20582	0,04568	0,03569	0,001
Cu	0,01650	0,00143	0,00484	0,00089	0,00636	0,00266	0,00403	0,00102	0,00213	0,00107	0,00091	0,0005
Ni	0,07702	0,02963	0,02819	0,01722	0,01108	0,02261	0,01885	0,55600	0,06579	0,06311	0,02037	0,0001
Zn	0,25965	0,04593	0,01408	0,06337	0,10583	0,06775	0,06827	0,01804	0,01773	0,01460	0,00703	0,001
Ti	0,00148	0,00163	0,01748	0,00122	0,00042	0,00074	0,00382	0,00045	0,00106	0,00072	0,00056	0,0001
V	0,00570	0,00193	0,00707	0,00066	0,00736	0,00310	0,01108	0,00207	0,00254	0,00197	0,00171	0,00001
Cr	0,00245	0,00290	0,03978	0,00323	0,00310	0,00227	0,00624	0,00283	0,00285	0,00368	0,00463	0,0001
Mn	0,06109	0,22890	0,14390	1,30000	0,56331	0,08762	1,41000	0,10863	0,08586	0,08653	0,06861	0,00001
Co	0,00158	0,00078	0,00264	0,00106	0,00050	0,00083	0,00580	0,00148	0,00048	0,00031	0,00021	0,00001
As	0,00160	0,01584	0,01332	0,00217	0,00251	0,00069	0,00187	0,00799	0,00795	0,00793	0,00653	0,0001
Mo	0,01161	0,00723	0,00301	0,01638	0,00282	0,00130	0,00528	0,00317	0,00250	0,00190	0,00168	0,0005

ICP-MS- n.d.
ICP-MS- dilution 10x
ICP-OES- n.d.

(a) Water samples

Conc [ug/kg]	TEP sed 1	TEP sed 3	TEP sed 4	TEP 5.1	TEP 5.2	MB1 sol	MB2 sed	MB3 sed	MB9 sol	MB5 sed	MB7 sed	LOQ
Pb	18 235	5 895	4 718	1 567	3 493	7 957	8 007	24 727	69 699	2 012	8 172	5
Cd	<LOQ	<LOQ	<LOQ	55	80	226	160	163	1 730	<LOQ	152	50
Fe	64 982 610	1 691 661	2 242 654	1 718 673	2 496 329	1 643 796	1 294 752	2 960 692	6 688 480	993 510	5 429 606	2 500
Cu	15 319	1 117	2 136	1 001	2 717	8 157	70 332	7 810	90 009	1 757	8 083	50
Ni	23 403	976	1 383	1 944	2 491	1 960	4 034	2 546	16 501	1 161	6 676	50
Zn	60 306	8 275	11 498	4 654	13 333	54 772	62 867	48 514	202 034	8 138	42 525	2 500
Ti	566 028	120 365	120 870	134 581	186 029	167 664	72 060	96 873	215 591	136 886	305 561	250
Cr	207 589	3 292	4 260	5 152	7 426	5 315	3 658	7 185	17 564	4 491	19 867	250
Mn	152 966	128 497	103 693	28 916	35 175	27 893	15 891	73 445	17 542	13 109	53 959	5
Co	5 561	465	622	608	782	739	396	817	2 526	276	1 577	5
As	11 322	503	671	483	671	378	659	1 102	802	225	1 258	5
Mo	<LOQ	268	392	<LOQ	415	513	<LOQ	<LOQ	720	<LOQ	349	250
V	199 733	4 034	4 790	3 685	5 678	3 470	1 986	3 839	8 083	2 797	14 516	5

ICP-MS- dilution 10x
ICP-MS- dilution 100x
ICP-MS- dilution 1000x
ICP-OES- dilution 10x

(b) Soil and sediment samples

Conc (mg/kg)	MB1	MB8	MB9	MB10	LOQ
Pb	5,97	46,07	55,92	71,53	0,02
Fe	232,22	807,02	287,99	370,76	10
Cu	11,69	17,96	5,70	3,11	0,2
Ni	0,71	6,51	1,89	1,96	0,2
Zn	7611,46	18474,63	9559,28	9732,55	10
Ti	28,33	57,59	18,14	14,11	1
V	0,90	1,77	0,67	0,68	0,02
Cr	6,02	11,68	10,17	5,37	1
Mn	2,68	7,89	2,97	3,52	0,02
Co	0,15	0,38	0,59	0,24	0,02
Mo	<LOQ	<LOQ	<LOQ	<LOQ	1

ICP-MS- dilution 10x
ICP-OES- dilution 10x

(c) Tire samples

Figure 27: Details about instrumental analysis, dilution factor and limit of quantification of metal concentrations

D PAHs and PCBs concentrations

Table 18: PAHs and PCBs concentrations in soil and sediments samples from Technopole and Mbeubeuss sites.

	Technopole					Mbeubeuss						TEC[a]	PEC[b]	ISQG[c]	PEL[d]
	TEP1 sed	TEP3 sed	TEP4 sed	TEP5.1 s	TEP5.2 s	MB1 s	MB2 sed	MB3 sed	MB9 s	MB5 sed	MB7 sed				
PAHs concentration [ng/g]															
Antracene	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	57,2	845	46,9	245
Benzo(a)anthracene	0,60	0,00	0,00	0,00	D	D	0,00	0,00	D	0,00	0,21	108	1050	31,7	385
Benzo (a) pyrene	5,13	0,00	0,00	0,00	D	0,00	0,00	0,00	0,00	0,00	1,99	150	1450	31,9	782
Benzo (b) fluoranthene	0,53	0,00	0,00	0,00	0,15	D	0,00	0,11	0,24	0,00	0,20				
Benzo (e) pyrene	4,93	0,00	0,00	0,00	D	0,00	0,00	0,00	D	0,00	1,74				
Benzo (g,h,i) perylene	55,03	0,00	0,00	0,00	D	D	0,00	21,94	D	0,00	22,79				
Benzo (k) fluoranthene	0,12	0,00	0,00	0,00	D	0,00	0,00	0,00	D	0,00	D				
Chrysene	1,13	0,00	D	0,00	0,36	0,43	D	0,28	1,03	0,00	0,59	166	1290	57,1	862
Dibenzo (a,h) anthracene	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	33		6,22	135
Fluoranthene	1,61	0,36	0,49	0,33	0,89	0,61	1,13	0,39	1,63	0,43	0,50	423	2230	111	2355
Fluorene	0,00	0,00	0,00	0,00	0,00	D	0,00	D	0,00	0,00	0,00	77,4	536	21,2	144
Indeno (1,2,3-cd) pyrene	0,03	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,01				
Phenanthrene	26,09	10,67	11,66	10,37	12,14	14,50	34,53	9,55	29,12	9,98	15,71	204	1170	41,9	515
Pyrene	1,22	0,30	0,35	D	0,74	0,43	D	0,30	1,04	D	0,73	195	1520	53	875
Σ14 HAPs	96,42	11,33	12,50	10,70	14,28	15,97	35,66	32,57	33,06	10,41	44,47				
Σ13 HAPs [e]	96,39	11,33	12,50	10,70	14,28	15,97	35,66	32,57	33,06	10,41	44,46	1610	22800		
PCBs concentration [ng/g]															
CB 101	D	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00				
CB 128	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00				
CB 138	1,56	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00				
CB 149	0,61	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	D				
CB 153	1,07	0,00	0,00	0,00	0,00	0,00	0,00	D	0,00	0,00	0,00				
CB 170	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00				
CB 180	1,14	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00				
CB 28	D	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00				
CB 52	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00				
Σ9 PCBs	4,38	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00				
Total PCBs (Σ7 x 4.3)	16,19	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	59,8	676	34,1	277

[a] *Threshold effect concentration (TEC) proposed by Macdonald et al.*

[b] *Probable effect concentration (PEC) proposed by Macdonald et al.*

[c] *Cell are colored in red if above ISQG proposed by Canadian Council of Ministers of the Environment.*

[d] *Values are in red if above probable effect level (PEL) proposed by Canadian Council of Ministers of the Environment.*

[e] *Indeno(1,2,3-cd)pyrene is not included in the sum.*

The PCBs and PAHs congeners analysed by GC-MS/MS were the following:

Table 19: List of analysed PCBs and PAHs by GC-MS/MS.

PCB congener	associated ISTD
PCB 28	PCB 28-C13
PCB 52	PCB 52-C13
PCB 101	PCB 101-C13
PCB 149	PCB 153-C13
PCB 118 [a]	PCB 101-C13
PCB 153	PCB 153-C13
PCB 138	PCB 138-C13
PCB 128	PCB 128-C13
PCB 180	PCB 180-C13
PCB 170	PCB 170-C13
Antracene	Anthracene d10
Benzo(a)anthracene	Benzo(a)anthracene d12
Benzo(a)pyrene	Benzo(a)pyrene d12
Benzo(b)fluoranthene	Benzo(b)fluoranthene d12
Benzo(e)pyrene	Benzo(a)pyrene d12
Benzo(g,h,i)perylene	Benzo(g,h,i)perylene d12
Benzo(k)fluoranthene	Benzo(k)fluoranthene d12
Chrysene	Chrysene d12
Dibenzo(a,h)anthracene	Dibenzo(a,h)anthracene d14
Fluoranthene	Fluoranthene d10
Fluorene	Fluorene d10
Indeno(1,2,3-cd)pyrene	Indeno(1,2,3-cd)pyrene d12
Phenanthrene	Phenanthrene d10
Pyrene	Pyrene d10

[a] *Quantification was not possible due to a calibration curve of bad quality* ($R^2 < 0,97$).

E Tire related compounds concentration

E.1 Water samples

Table 20: Concentration of tire additives in water samples determined by SPE followed by LC-MS/MS.

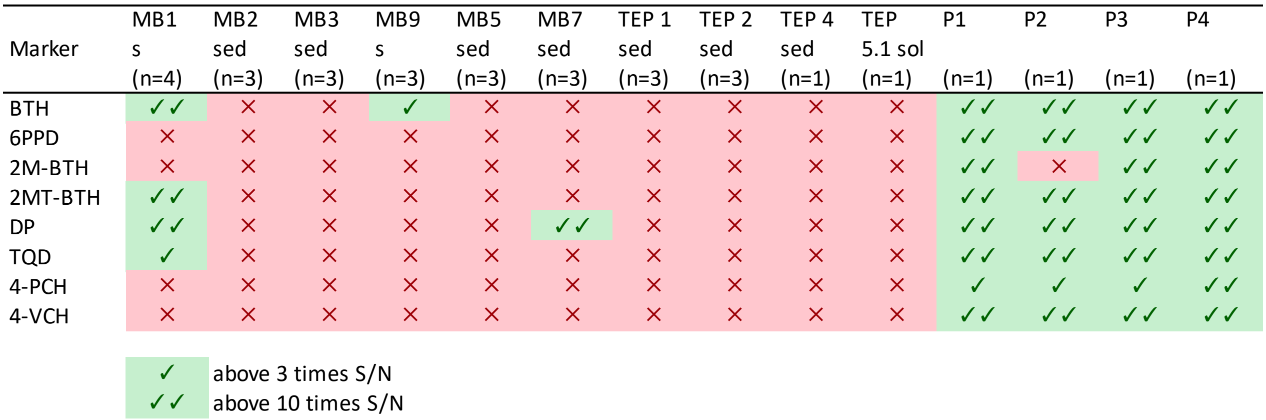
Tire additives [ng/mL]	Mbeubeuss							Technopole			
	MB1[a] rw	MB2 sw	MB3 sw	MB4 gw	M5 sw	MB6 gw	MB7 sw	TEP1 sw	TEP2 sw	TEP3 sw	TEP4[a] sw
AN	0,000	0,007	0,024	0,000	0,000	0,000	0,000	0,000	0,000	0,124	0,000
CHA	24,913	0,256	0,237	0,497	0,000	0,164	0,000	0,026	0,000	0,000	0,000
2-HBTH	6,139	0,000	0,222	0,000	0,112	0,328	0,000	0,000	0,000	0,000	0,000
BTH	0,000	1,111	0,971	0,502	0,000	1,801	0,000	0,000	0,000	0,000	0,000
2-ABTH	0,000	0,013	0,16	0,000	0,000	0,023	0,000	0,012	0,025	0,021	0,000
SBTH	0,000	0,066	0,041	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000
MTBT	0,000	0,834	0,069	0,178	0,024	0,055	0,000	0,000	0,000	0,027	0,000
6PPD Q	0,000	0,038	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000

[a] *Sample MB1 and TEP4 were analysed by direct injection in LC-MS/MS due to loss of samples (the bottles were broken during transport).*

E.2 Soil and sediment samples

Table 21: Benzothiazole concentration [ng/kg] in soil and sediment samples extracted by ASE and analysed by LC-HRMS.

BTH [ng/kg]	MB1 s	MB2 sed	MB3 sed	MB9 s	TEP1 sed	TEP4 sed	TEP5.1 s	TEP5.2 s
Mean	12,20	3,22	0,80	2,20	0,96	1,23	0,74	1,52
Std	±0,77	±0,73	±0,74	±0,63	±0,83	±0,71	±0,64	±0,42



Marker	MB1 s (n=4)	MB2 sed (n=3)	MB3 sed (n=3)	MB9 s (n=3)	MB5 sed (n=3)	MB7 sed (n=3)	TEP 1 sed (n=3)	TEP 2 sed (n=3)	TEP 4 sed (n=1)	TEP 5.1 sol (n=1)	P1 (n=1)	P2 (n=1)	P3 (n=1)	P4 (n=1)
BTH	✓✓	×	×	✓	×	×	×	×	×	×	✓✓	✓✓	✓✓	✓✓
6PPD	×	×	×	×	×	×	×	×	×	×	✓✓	✓✓	✓✓	✓✓
2M-BTH	×	×	×	×	×	×	×	×	×	×	✓✓	×	✓✓	✓✓
2MT-BTH	✓✓	×	×	×	×	×	×	×	×	×	✓✓	✓✓	✓✓	✓✓
DP	✓✓	×	×	×	×	✓✓	×	×	×	×	✓✓	✓✓	✓✓	✓✓
TQD	✓	×	×	×	×	×	×	×	×	×	✓✓	✓✓	✓✓	✓✓
4-PCH	×	×	×	×	×	×	×	×	×	×	✓	✓	✓	✓✓
4-VCH	×	×	×	×	×	×	×	×	×	×	✓✓	✓✓	✓✓	✓✓

✓ above 3 times S/N
✓✓ above 10 times S/N

Figure 28: Results of analysis of tire pyrolysis markers by Pyr-GC-MS

F Details regarding analyses of tire related compounds with LC-MS/MS, LC-HRMS Orbitrap and pyr-GC-MS

F.1 Analyses of water samples on LC-MS/MS

F.1.1 Solid phase extraction recovery

SPE recovery tests experiment

SPE recovery tests were conducted for the tire additives by spiking 50 mL of MilliQ water with 50 μl of a mix of analytes at 1000 ng/ml and 50 μl of associated internal standards (732 ng/ml 6PPDQ-d5, 10080 ng/ml BT-d4, 510 ng/ml DPU-d10 and 746 ng/ml Aniline-d5) and extracting following the SPE protocol described in section 2.4.1. Suitable recoveries for most targets were obtained with an overall mean of $59 \pm 21\%$ with an external calibration curve. CHA and S-BTH were not correctly detected in standards, therefore nothing could be deduced from their calibration curves and 6-PPD values were below detection limit. Analytes recoveries after surrogates' correction (i.e. using internal calibration curves) were high, with an overall mean of $152 \pm 55\%$. This means that calculated concentrations may be over estimated for some compounds by a factor ranging from 1.06 for 6PPD-Q to 2.3 for 2-HBTH, according to the results, while MTBT could be underestimated (0.9). This could be explain by the fact that each analyte is not associated with its corresponding deuterated compound, due to lack of availability. Indeed, the worse results (far from 100% recovery) are obtained for 2-HBTH (230 %) and 2-ABTH (224 %), whose internal standard is a deuterated benzothiazole (BTH-d4) despite a potential difference in affinity with the cartridge and the eluent due to their specific structure (see figure 29).

Table 22: Recoveries [%] of tire additives in test samples (miliQ spiked with tire additives)

Compound	AN	CHA	2-HBTH	BTH	2-ABTH	SBTH	MTBT	DPG	6PPD	6PPD-Q
Test 1.1	132	prob. cal.	231	148	221	prob. cal.	92	130	n.d.	110
Test 1.2	131		282	154	270		88	121		103
Test 1.3	119		175	168	181		91	143		106
Mean	127		230	156	224		90	131		106
Stdv	±7		±53	±10	±44		±2	±11		±3

(a) Overall recoveries [%] of compounds

Compound	AN	CHA	2-HBTH	BTH	2-ABTH	SBTH	MTBT	DPG	6PPD	6PPD-Q
Test 1.1	41	prob. cal.	80	52	77	prob. cal.	32	79	n.d.	44
Test 1.2	37		79	43	76		25	75		42
Test 1.3	38		83	80	87		43	81		39
Mean	39		81	58	80		34	79		42
Stdv	±2		±2	±19	±6		±9	±3		±3

(b) Recoveries [%] of compounds without surrogates' correction

Surrogate	AN-d5	BTH-d4	DPU-d10	6PPDQ-d5
Mean	28	37	60	37
Stdv	±4	±3	±10	±2

(c) Recoveries [%] of surrogates

The surrogate associated with each compound is as follow: AN-d5 for AN and CHA, BTH-d4 for 2-HBTH, BTH, 2-ABTH, SBTH and MTBT, DPU-d10 for DPG and 6PPDQ-d5 for 6PPD and 6PPDQ. Stdv stands for standard deviation, n.d for not detected (6-PPD) and prob. cal. means there was a problem with calibration curve and nothing could be deduced from it (MTBS, CHA and S-BTH).

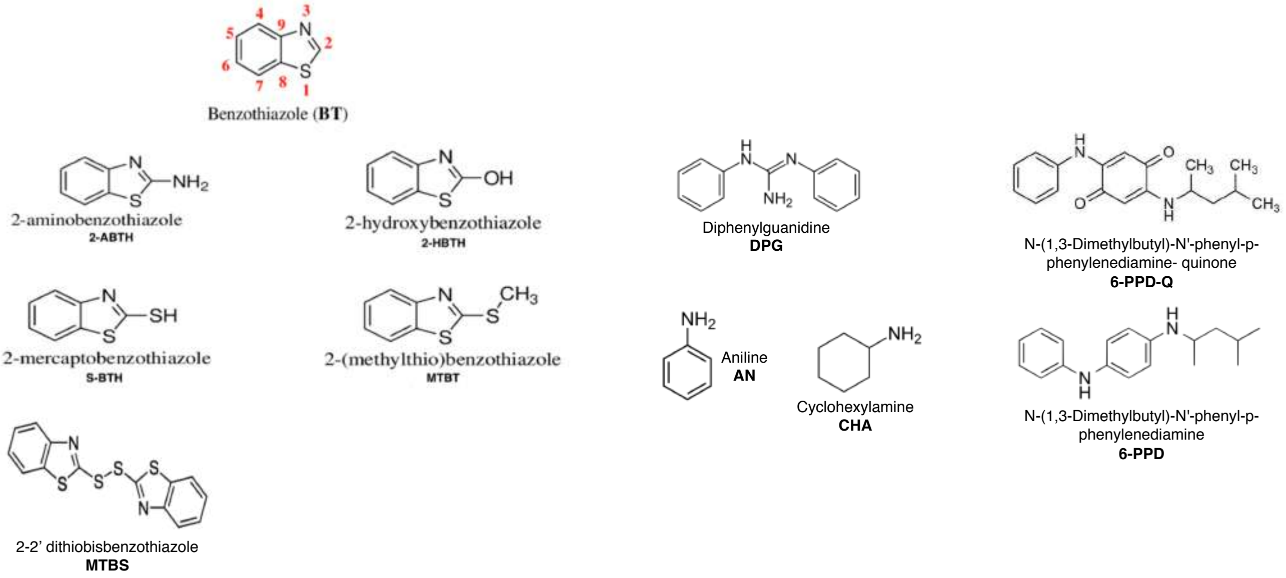


Figure 29: Tire additive chemicals

SPE recovery of water samples

The following table shows the surrogates' recoveries obtained for the spiked water samples. Recoveries values are below the ones obtained for test samples (table 22c), especially for AN-d5 (9 ± 6%) and 6PPDQ-d5 16 ± 9%, which are not suitable results. BTH-d4 and DPU-d10 recoveries are appropriate for the calculation of tire additive concentrations (>30 %) but as mentioned above, under- or overestimation may be possible.

Table 23: Recoveries [%] of surrogates in collected water samples

Surrogate	AN-d5	BTH-d4	DPU-d10	6PPDQ-d5
MB2	13	31	52	20
MB3	13	26	41	15
MB4	3	41	55	10
MB5	21	56	64	33
MB6	9	35	56	13
MB7	6	35	51	12
TEP1	9	19	25	11
TEP2	1	18	30	7
TEP3	9	51	82	27
Mean	9	35	51	16
Stdv	±6	±13	±18	±9

F.1.2 Method blank and quantification limit of LC-MS/MS analysis

Method blank, consisting of 100 mL of MilliQ, showed an high contamination with areas values between the first and third standard for additives AN, CHA, 2-HBTH and DPG. In order to determine if there is a constant contamination, the operation was repeated by extracting two samples in triplicate: 100 mL of Ultrapure MilliQ and 100 mL of tap water spiked with ISTD (Table 24). Values were lower but still of the same order of magnitude than the first standard, therefore mean blank area has been systematically subtracted from sample areas to correct for potential contamination and avoid over estimation. By doing this, only a few additives from a few samples were above the quantification limit, defined as the the highest standard being above a signal to noise ratio of ten.

Table 24: Method blank's areas obtained by LC-MS/MS.

Area	AN	CHA	2-HBTH	BTH	DPG
MilliQ (n=1)	4'573	866	1'799	68	543'955
Ultra pure MilliQ (n=3)	2'366 ±771	337 ±152	331 ±375	55 ±35	19'709 ±2'405
Tap water (n=3)	900 ±11	585 ±197	251 ±193	151 ±111	13'593 ±3'478
Method blank mean	2'613	596	794	91	192'419
Standard 1	1'791	785	493	76	16'919
Standard 2	9'047	3'316	1'641	134	81'727
Standard 3	18'259	6'579	2'260	260	162'882
Standard 4	86'656	30'205	12'350	946	756'598

Table 25: Limits of quantification for the analysis of tire additives in water samples by LC-MS/MS.

LOQs [ng/ml]	AN	CHA	2-HBTH	BTH	2-ABTH	SBTH	MTBT	DPG	6PPD	6PPD Q
MB2/3/4/5/6, TEP1/2/3 [a]	0,124	0,497	0,328	1,801	0,16	0,066	0,834	0,398	0,003	0,038
MB1, TEP4 [b]	1,29	4,38	6,14	44,1	1,43	4,62	1,6	2,09	0,77	0,9

[a] *Solid phase extraction followed by LC-MS/MS.*
[b] *Direct injection in LC-MS/MS.*

F.2 Analysis of soil and sediment samples on pyr-GC-MS

Pyrolyser Mode:double shot/ TED conditions: 100 °C, 0 min, 30°C/min, 3 min. (interface 300°C)/ Pyrolysis conditions: 700 °C, 0.2min

GC Column: Ultra Alloy-5 (30mx0.25mmx0.25um+0.7mx150umx0m)/ Oven: 50°C, 2min, 5°C/min, 160°C, 0min, 15°C/min, 300°C, 5.66mmin, T=39min/ Inlet: 300 °C, split= 50ml/min, ratio= 50:1, fixed flow rate= 1ml/min/ Transfer line: 300 °C

MS Mode: el pos 70/ Source=:230°/ Quad:150°C / Delay:3 min

F.2.1 Secondary analysis by Pyr-GC-MS

Before targeting pyrolysis products of tires, a general scan of triplicates of 20 mg of a selection of samples was performed with soil MB1 due to its vicinity to tires dumping site as well as with soil MB5.1 and sediment TEP4 because of their vicinity to important roads. No peaks corresponding to tire rubber or additives were observed. Therefore, a second experiment was conducted by monitoring ions of interest at appropriate retention time in order to gain some precision and to identify, if present, pyrolysis products of tires. 20 mg of the same samples were analysed in one replicate and results showed the presence of some of the pyrolysis markers. To ensure the suitability of the method, 1 mg powder of each tire sample from the landfill of Mbeubeuss was also analysed. Pyrolysis markers' signal was above 3 times the signal to noise ratio for each sample, with the exception of 2M-BTH in tire sample MB8. Results are given in table 28.

Given that the peak areas of the pyrolysis markers were in most cases below three times the signal to noise ratio, we tried to increase the sample mass to see if higher sensitivity could be obtain. Triplicates of 30 mg of sample MB1 were placed into pyrolysis cup and analysed. No significant increase in relative signal area (compared to noise) was observed.

G Details about non-target LC-HRMS analysis

G.1 Non-target analysis

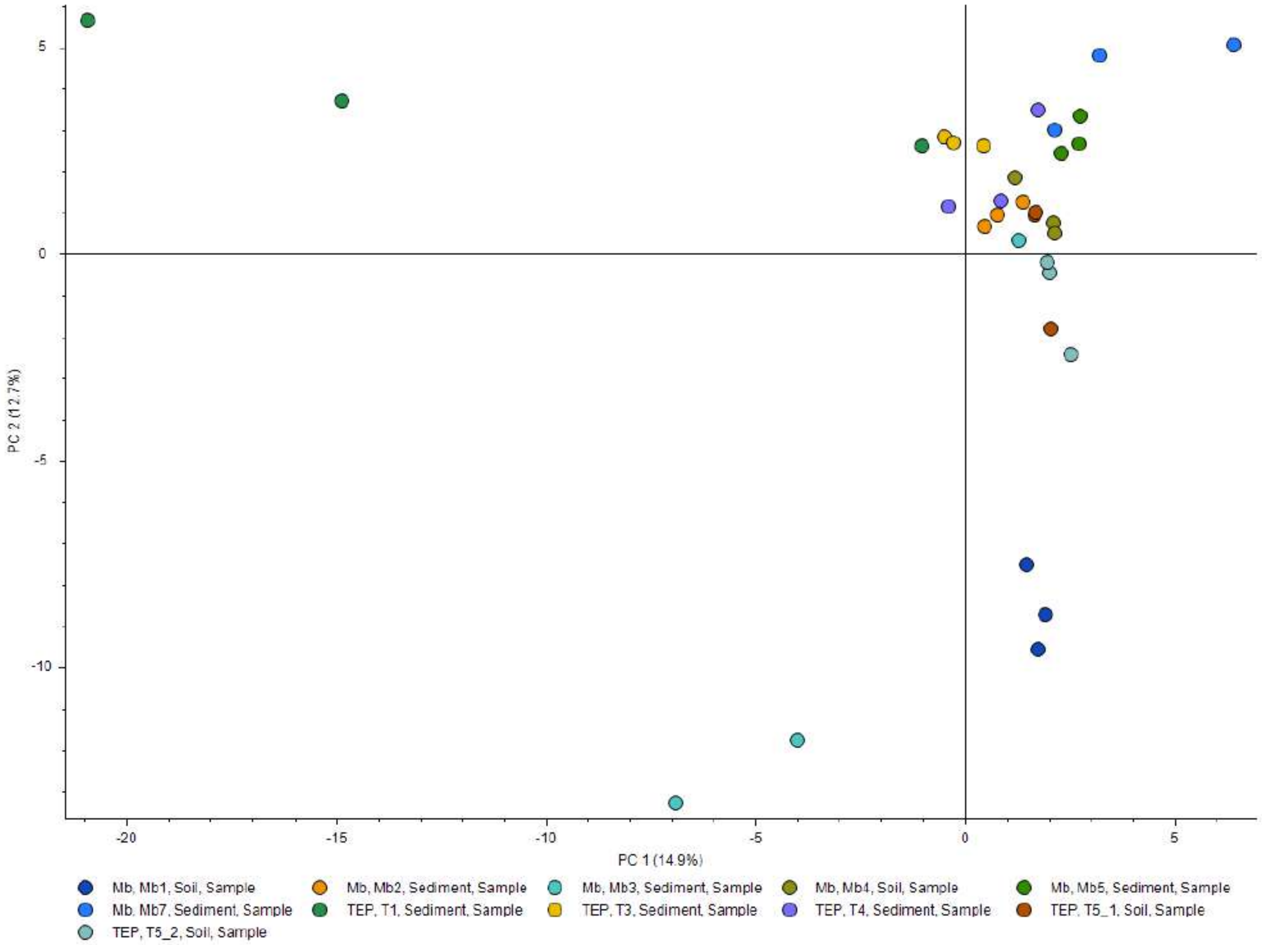
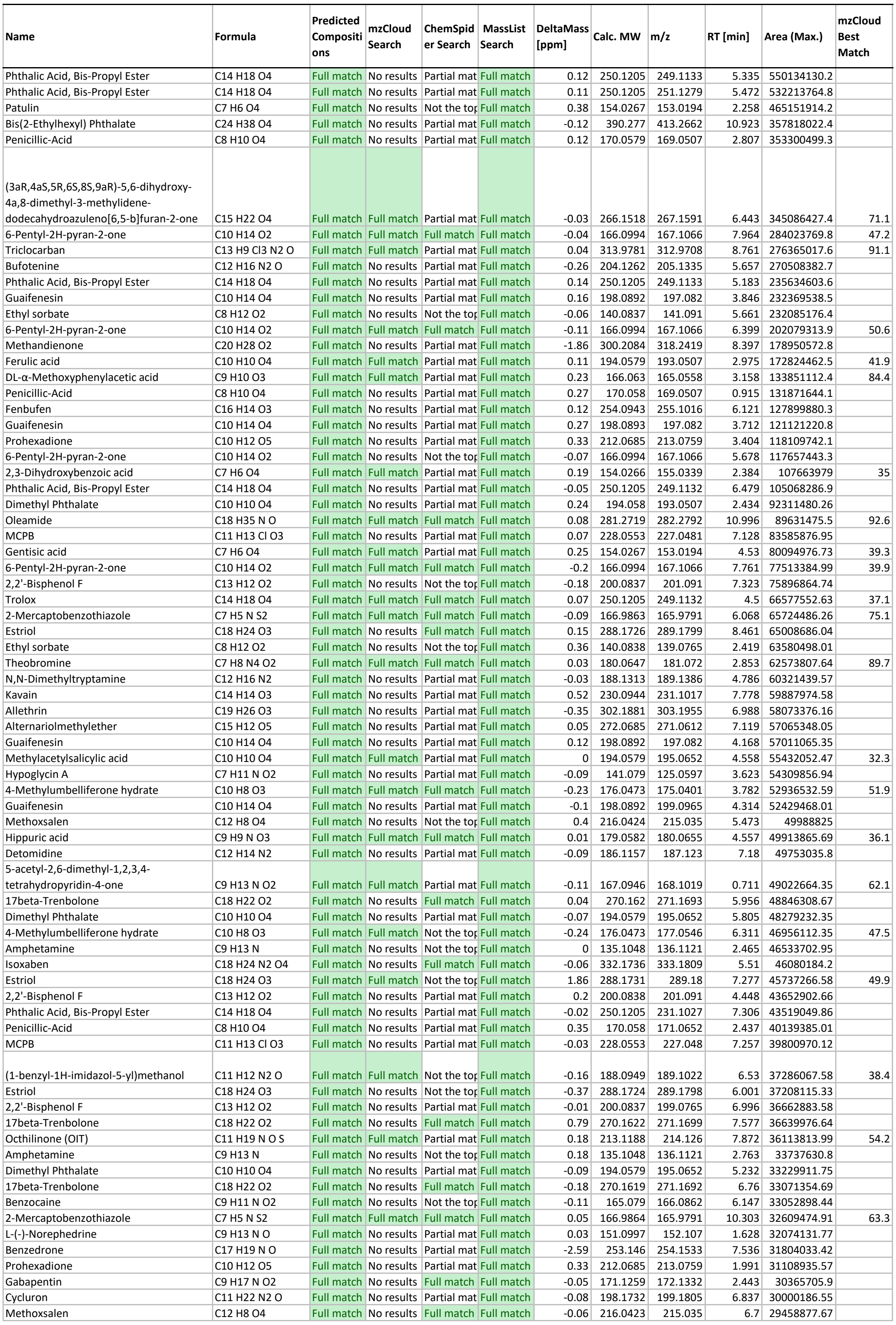
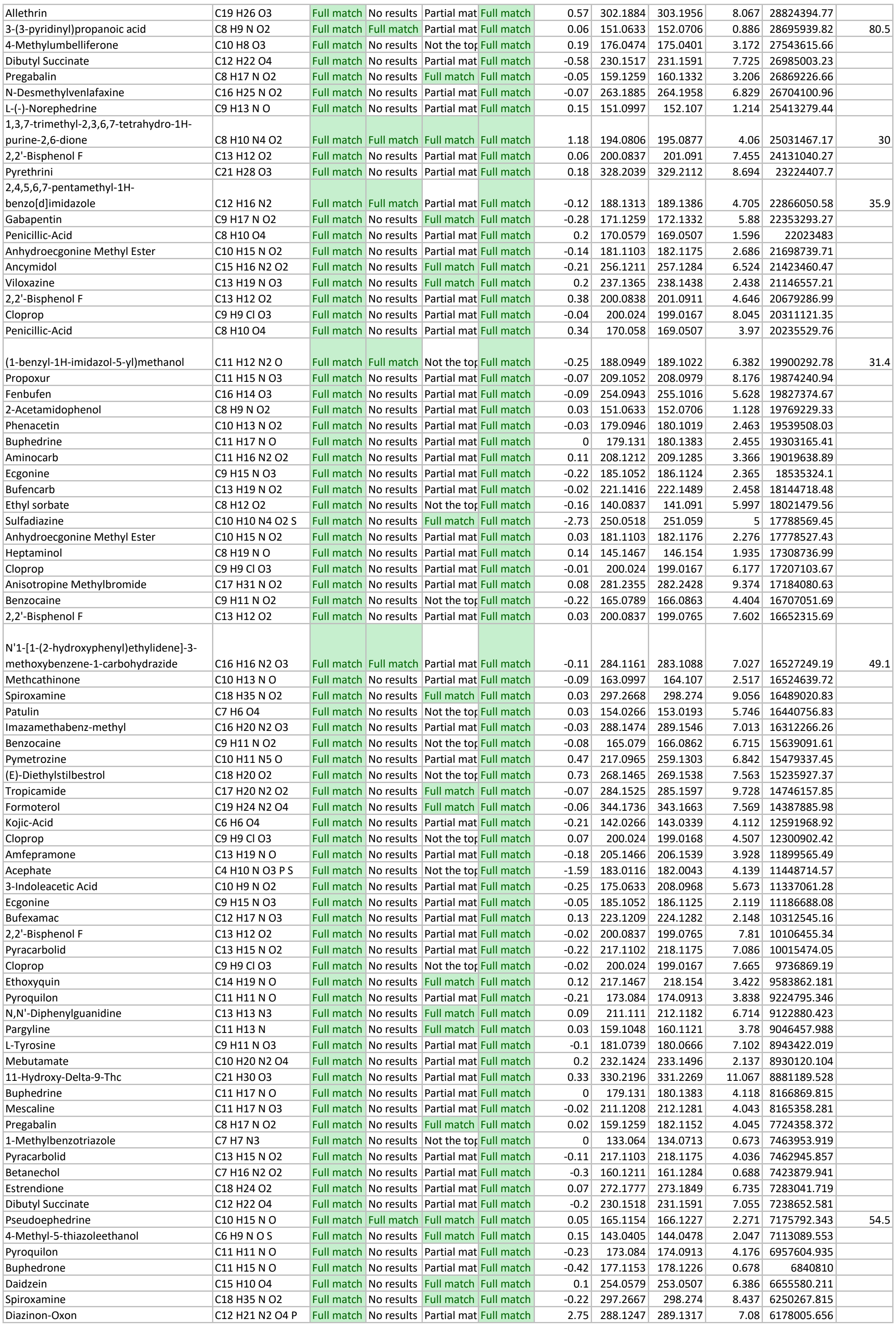


Figure 30: Principal components based on the 170 compounds selected after the filtering steps (see Figure 33).



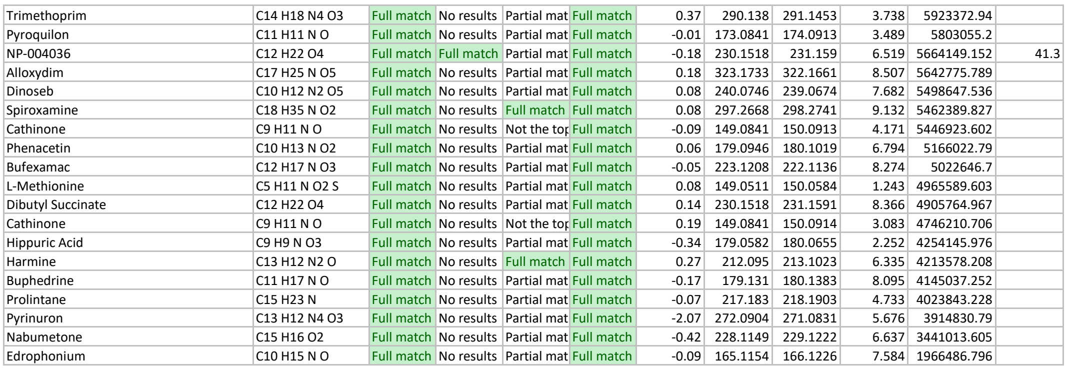
Name	Formula	Predicted Compositions	mzCloud Search	ChemSpider Search	MassList Search	DeltaMass [ppm]	Calc. MW	m/z	RT [min]	Area (Max.)	mzCloud Best Match
Phthalic Acid, Bis-Propyl Ester	C14 H18 O4	Full match	No results	Partial mat	Full match	0.12	250.1205	249.1133	5.335	550134130.2	
Phthalic Acid, Bis-Propyl Ester	C14 H18 O4	Full match	No results	Partial mat	Full match	0.11	250.1205	251.1279	5.472	532213764.8	
Patulin	C7 H6 O4	Full match	No results	Not the top	Full match	0.38	154.0267	153.0194	2.258	465151914.2	
Bis(2-Ethylhexyl) Phthalate	C24 H38 O4	Full match	No results	Partial mat	Full match	-0.12	390.277	413.2662	10.923	357818022.4	
Penicillic-Acid	C8 H10 O4	Full match	No results	Partial mat	Full match	0.12	170.0579	169.0507	2.807	353300499.3	
(3aR,4aS,5R,6S,8S,9aR)-5,6-dihydroxy-4a,8-dimethyl-3-methylidene-dodecahydroazuleno[6,5-b]furan-2-one	C15 H22 O4	Full match	Full match	Partial mat	Full match	-0.03	266.1518	267.1591	6.443	345086427.4	71.1
6-Pentyl-2H-pyran-2-one	C10 H14 O2	Full match	Full match	Full match	Full match	-0.04	166.0994	167.1066	7.964	284023769.8	47.2
Triclocarban	C13 H9 Cl3 N2 O	Full match	Full match	Partial mat	Full match	0.04	313.9781	312.9708	8.761	276365017.6	91.1
Bufotenine	C12 H16 N2 O	Full match	No results	Partial mat	Full match	-0.26	204.1262	205.1335	5.657	270508382.7	
Phthalic Acid, Bis-Propyl Ester	C14 H18 O4	Full match	No results	Partial mat	Full match	0.14	250.1205	249.1133	5.183	235634603.6	
Guaifenesin	C10 H14 O4	Full match	No results	Partial mat	Full match	0.16	198.0892	197.082	3.846	232369538.5	
Ethyl sorbate	C8 H12 O2	Full match	No results	Not the top	Full match	-0.06	140.0837	141.091	5.661	232085176.4	
6-Pentyl-2H-pyran-2-one	C10 H14 O2	Full match	Full match	Full match	Full match	-0.11	166.0994	167.1066	6.399	202079313.9	50.6
Methandienone	C20 H28 O2	Full match	No results	Partial mat	Full match	-1.86	300.2084	318.2419	8.397	178950572.8	
Ferulic acid	C10 H10 O4	Full match	Full match	Partial mat	Full match	0.11	194.0579	193.0507	2.975	172824462.5	41.9
DL-α-Methoxyphenylacetic acid	C9 H10 O3	Full match	Full match	Partial mat	Full match	0.23	166.063	165.0558	3.158	133851112.4	84.4
Penicillic-Acid	C8 H10 O4	Full match	No results	Partial mat	Full match	0.27	170.058	169.0507	0.915	131871644.1	
Fenbufen	C16 H14 O3	Full match	No results	Partial mat	Full match	0.12	254.0943	255.1016	6.121	127899880.3	
Guaifenesin	C10 H14 O4	Full match	No results	Partial mat	Full match	0.27	198.0893	197.082	3.712	121121220.8	
Prohexadione	C10 H12 O5	Full match	No results	Partial mat	Full match	0.33	212.0685	213.0759	3.404	118109742.1	
6-Pentyl-2H-pyran-2-one	C10 H14 O2	Full match	No results	Not the top	Full match	-0.07	166.0994	167.1066	5.678	117657443.3	
2,3-Dihydroxybenzoic acid	C7 H6 O4	Full match	Full match	Partial mat	Full match	0.19	154.0266	155.0339	2.384	107663979	35
Phthalic Acid, Bis-Propyl Ester	C14 H18 O4	Full match	No results	Partial mat	Full match	-0.05	250.1205	249.1132	6.479	105068286.9	
Dimethyl Phthalate	C10 H10 O4	Full match	No results	Partial mat	Full match	0.24	194.058	193.0507	2.434	92311480.26	
Oleamide	C18 H35 N O	Full match	Full match	Full match	Full match	0.08	281.2719	282.2792	10.996	89631475.5	92.6
MCPB	C11 H13 Cl O3	Full match	No results	Partial mat	Full match	0.07	228.0553	227.0481	7.128	83585876.95	
Gentisic acid	C7 H6 O4	Full match	Full match	Partial mat	Full match	0.25	154.0267	153.0194	4.53	80094976.73	39.3
6-Pentyl-2H-pyran-2-one	C10 H14 O2	Full match	Full match	Full match	Full match	-0.2	166.0994	167.1066	7.761	77513384.99	39.9
2,2'-Bisphenol F	C13 H12 O2	Full match	No results	Not the top	Full match	-0.18	200.0837	201.091	7.323	75896864.74	
Trolox	C14 H18 O4	Full match	Full match	Full match	Full match	0.07	250.1205	249.1132	4.5	66577552.63	37.1
2-Mercaptobenzothiazole	C7 H5 N S2	Full match	Full match	Full match	Full match	-0.09	166.9863	165.9791	6.068	65724486.26	75.1
Estriol	C18 H24 O3	Full match	No results	Full match	Full match	0.15	288.1726	289.1799	8.461	65008686.04	
Ethyl sorbate	C8 H12 O2	Full match	No results	Not the top	Full match	0.36	140.0838	139.0765	2.419	63580498.01	
Theobromine	C7 H8 N4 O2	Full match	Full match	Full match	Full match	0.03	180.0647	181.072	2.853	62573807.64	89.7
N,N-Dimethyltryptamine	C12 H16 N2	Full match	No results	Partial mat	Full match	-0.03	188.1313	189.1386	4.786	60321439.57	
Kavain	C14 H14 O3	Full match	No results	Partial mat	Full match	0.52	230.0944	231.1017	7.778	59887974.58	
Allethrin	C19 H26 O3	Full match	No results	Partial mat	Full match	-0.35	302.1881	303.1955	6.988	58073376.16	
Alternariolmethylether	C15 H12 O5	Full match	No results	Partial mat	Full match	0.05	272.0685	271.0612	7.119	57065348.05	
Guaifenesin	C10 H14 O4	Full match	No results	Partial mat	Full match	0.12	198.0892	197.082	4.168	57011065.35	
Methylacetylsalicylic acid	C10 H10 O4	Full match	Full match	Partial mat	Full match	0	194.0579	195.0652	4.558	55432052.47	32.3
Hypoglycin A	C7 H11 N O2	Full match	No results	Partial mat	Full match	-0.09	141.079	125.0597	3.623	54309856.94	
4-Methylumbelliferone hydrate	C10 H8 O3	Full match	Full match	Full match	Full match	-0.23	176.0473	175.0401	3.782	52936532.59	51.9
Guaifenesin	C10 H14 O4	Full match	No results	Partial mat	Full match	-0.1	198.0892	199.0965	4.314	52429468.01	
Methoxsalen	C12 H8 O4	Full match	No results	Not the top	Full match	0.4	216.0424	215.035	5.473	49988825	
Hippuric acid	C9 H9 N O3	Full match	Full match	Full match	Full match	0.01	179.0582	180.0655	4.557	49913865.69	36.1
Detomidine	C12 H14 N2	Full match	No results	Partial mat	Full match	-0.09	186.1157	187.123	7.18	49753035.8	
5-acetyl-2,6-dimethyl-1,2,3,4-tetrahydropyridin-4-one	C9 H13 N O2	Full match	Full match	Partial mat	Full match	-0.11	167.0946	168.1019	0.711	49022664.35	62.1
17beta-Trenbolone	C18 H22 O2	Full match	No results	Full match	Full match	0.04	270.162	271.1693	5.956	48846308.67	
Dimethyl Phthalate	C10 H10 O4	Full match	No results	Partial mat	Full match	-0.07	194.0579	195.0652	5.805	48279232.35	
4-Methylumbelliferone hydrate	C10 H8 O3	Full match	Full match	Not the top	Full match	-0.24	176.0473	177.0546	6.311	46956112.35	47.5
Amphetamine	C9 H13 N	Full match	No results	Not the top	Full match	0	135.1048	136.1121	2.465	46533702.95	
Isoxaben	C18 H24 N2 O4	Full match	No results	Full match	Full match	-0.06	332.1736	333.1809	5.51	46080184.2	
Estriol	C18 H24 O3	Full match	Full match	Not the top	Full match	1.86	288.1731	289.18	7.277	45737266.58	49.9
2,2'-Bisphenol F	C13 H12 O2	Full match	No results	Partial mat	Full match	0.2	200.0838	201.091	4.448	43652902.66	
Phthalic Acid, Bis-Propyl Ester	C14 H18 O4	Full match	No results	Partial mat	Full match	-0.02	250.1205	231.1027	7.306	43519049.86	
Penicillic-Acid	C8 H10 O4	Full match	No results	Partial mat	Full match	0.35	170.058	171.0652	2.437	40139385.01	
MCPB	C11 H13 Cl O3	Full match	No results	Partial mat	Full match	-0.03	228.0553	227.048	7.257	39800970.12	
(1-benzyl-1H-imidazol-5-yl)methanol	C11 H12 N2 O	Full match	Full match	Not the top	Full match	-0.16	188.0949	189.1022	6.53	37286067.58	38.4
Estriol	C18 H24 O3	Full match	No results	Not the top	Full match	-0.37	288.1724	289.1798	6.001	37208115.33	
2,2'-Bisphenol F	C13 H12 O2	Full match	No results	Partial mat	Full match	-0.01	200.0837	199.0765	6.996	36662883.58	
17beta-Trenbolone	C18 H22 O2	Full match	No results	Full match	Full match	0.79	270.1622	271.1699	7.577	36639976.64	
Octhilinone (OIT)	C11 H19 N O S	Full match	Full match	Partial mat	Full match	0.18	213.1188	214.126	7.872	36113813.99	54.2
Amphetamine	C9 H13 N	Full match	No results	Not the top	Full match	0.18	135.1048	136.1121	2.763	33737630.8	
Dimethyl Phthalate	C10 H10 O4	Full match	No results	Partial mat	Full match	-0.09	194.0579	195.0652	5.232	33229911.75	
17beta-Trenbolone	C18 H22 O2	Full match	No results	Full match	Full match	-0.18	270.1619	271.1692	6.76	33071354.69	
Benzocaine	C9 H11 N O2	Full match	No results	Not the top	Full match	-0.11	165.079	166.0862	6.147	33052898.44	
2-Mercaptobenzothiazole	C7 H5 N S2	Full match	Full match	Full match	Full match	0.05	166.9864	165.9791	10.303	32609474.91	63.3
L-(-)-Norephedrine	C9 H13 N O	Full match	No results	Partial mat	Full match	0.03	151.0997	152.107	1.628	32074131.77	
Benzedrone	C17 H19 N O	Full match	No results	Partial mat	Full match	-2.59	253.146	254.1533	7.536	31804033.42	
Prohexadione	C10 H12 O5	Full match	No results	Partial mat	Full match	0.33	212.0685	213.0759	1.991	31108935.57	
Gabapentin	C9 H17 N O2	Full match	No results	Full match	Full match	-0.05	171.1259	172.1332	2.443	30365705.9	
Cycluron	C11 H22 N2 O	Full match	No results	Partial mat	Full match	-0.08	198.1732	199.1805	6.837	30000186.55	
Methoxsalen	C12 H8 O4	Full match	No results	Full match	Full match	-0.06	216.0423	215.035	6.7	29458877.67	

Figure 31: Tentative candidates for the features selected after the filtering steps (1).



Allethrin	C19 H26 O3	Full match	No results	Partial mat	Full match	0.57	302.1884	303.1956	8.067	28824394.77	
3-(3-pyridinyl)propanoic acid	C8 H9 N O2	Full match	Full match	Partial mat	Full match	0.06	151.0633	152.0706	0.886	28695939.82	80.5
4-Methylumbelliferone	C10 H8 O3	Full match	No results	Not the top	Full match	0.19	176.0474	175.0401	3.172	27543615.66	
Dibutyl Succinate	C12 H22 O4	Full match	No results	Partial mat	Full match	-0.58	230.1517	231.1591	7.725	26985003.23	
Pregabalin	C8 H17 N O2	Full match	No results	Full match	Full match	-0.05	159.1259	160.1332	3.206	26869226.66	
N-Desmethylvenlafaxine	C16 H25 N O2	Full match	No results	Partial mat	Full match	-0.07	263.1885	264.1958	6.829	26704100.96	
L-(-)-Norephedrine	C9 H13 N O	Full match	No results	Partial mat	Full match	0.15	151.0997	152.107	1.214	25413279.44	
1,3,7-trimethyl-2,3,6,7-tetrahydro-1H-purine-2,6-dione	C8 H10 N4 O2	Full match	Full match	Full match	Full match	1.18	194.0806	195.0877	4.06	25031467.17	30
2,2'-Bisphenol F	C13 H12 O2	Full match	No results	Partial mat	Full match	0.06	200.0837	201.091	7.455	24131040.27	
Pyrethrini	C21 H28 O3	Full match	No results	Partial mat	Full match	0.18	328.2039	329.2112	8.694	23224407.7	
2,4,5,6,7-pentamethyl-1H-benzo[d]imidazole	C12 H16 N2	Full match	Full match	Partial mat	Full match	-0.12	188.1313	189.1386	4.705	22866050.58	35.9
Gabapentin	C9 H17 N O2	Full match	No results	Full match	Full match	-0.28	171.1259	172.1332	5.88	22353293.27	
Penicillic-Acid	C8 H10 O4	Full match	No results	Partial mat	Full match	0.2	170.0579	169.0507	1.596	22023483	
Anhydroecgonine Methyl Ester	C10 H15 N O2	Full match	No results	Partial mat	Full match	-0.14	181.1103	182.1175	2.686	21698739.71	
Ancymidol	C15 H16 N2 O2	Full match	No results	Full match	Full match	-0.21	256.1211	257.1284	6.524	21423460.47	
Viloxazine	C13 H19 N O3	Full match	No results	Full match	Full match	0.2	237.1365	238.1438	2.438	21146557.21	
2,2'-Bisphenol F	C13 H12 O2	Full match	No results	Partial mat	Full match	0.38	200.0838	201.0911	4.646	20679286.99	
Cloprop	C9 H9 Cl O3	Full match	No results	Partial mat	Full match	-0.04	200.024	199.0167	8.045	20311121.35	
Penicillic-Acid	C8 H10 O4	Full match	No results	Partial mat	Full match	0.34	170.058	169.0507	3.97	20235529.76	
(1-benzyl-1H-imidazol-5-yl)methanol	C11 H12 N2 O	Full match	Full match	Not the top	Full match	-0.25	188.0949	189.1022	6.382	19900292.78	31.4
Propoxur	C11 H15 N O3	Full match	No results	Partial mat	Full match	-0.07	209.1052	208.0979	8.176	19874240.94	
Fenbufen	C16 H14 O3	Full match	No results	Partial mat	Full match	-0.09	254.0943	255.1016	5.628	19827374.67	
2-Acetamidophenol	C8 H9 N O2	Full match	No results	Partial mat	Full match	0.03	151.0633	152.0706	1.128	19769229.33	
Phenacetin	C10 H13 N O2	Full match	No results	Partial mat	Full match	-0.03	179.0946	180.1019	2.463	19539508.03	
Buphedrine	C11 H17 N O	Full match	No results	Partial mat	Full match	0	179.131	180.1383	2.455	19303165.41	
Aminocarb	C11 H16 N2 O2	Full match	No results	Partial mat	Full match	0.11	208.1212	209.1285	3.366	19019638.89	
Ecgonine	C9 H15 N O3	Full match	No results	Partial mat	Full match	-0.22	185.1052	186.1124	2.365	18535324.1	
Bufencarb	C13 H19 N O2	Full match	No results	Partial mat	Full match	-0.02	221.1416	222.1489	2.458	18144718.48	
Ethyl sorbate	C8 H12 O2	Full match	No results	Not the top	Full match	-0.16	140.0837	141.091	5.997	18021479.56	
Sulfadiazine	C10 H10 N4 O2 S	Full match	No results	Full match	Full match	-2.73	250.0518	251.059	5	17788569.45	
Anhydroecgonine Methyl Ester	C10 H15 N O2	Full match	No results	Partial mat	Full match	0.03	181.1103	182.1176	2.276	17778527.43	
Heptaminol	C8 H19 N O	Full match	No results	Partial mat	Full match	0.14	145.1467	146.154	1.935	17308736.99	
Cloprop	C9 H9 Cl O3	Full match	No results	Partial mat	Full match	-0.01	200.024	199.0167	6.177	17207103.67	
Anisotropine Methylbromide	C17 H31 N O2	Full match	No results	Partial mat	Full match	0.08	281.2355	282.2428	9.374	17184080.63	
Benzocaine	C9 H11 N O2	Full match	No results	Not the top	Full match	-0.22	165.0789	166.0863	4.404	16707051.69	
2,2'-Bisphenol F	C13 H12 O2	Full match	No results	Partial mat	Full match	0.03	200.0837	199.0765	7.602	16652315.69	
N'1-[1-(2-hydroxyphenyl)ethylidene]-3-methoxybenzene-1-carbohydrazide	C16 H16 N2 O3	Full match	Full match	Partial mat	Full match	-0.11	284.1161	283.1088	7.027	16527249.19	49.1
Methcathinone	C10 H13 N O	Full match	No results	Partial mat	Full match	-0.09	163.0997	164.107	2.517	16524639.72	
Spiroxamine	C18 H35 N O2	Full match	No results	Full match	Full match	0.03	297.2668	298.274	9.056	16489020.83	
Patulin	C7 H6 O4	Full match	No results	Not the top	Full match	0.03	154.0266	153.0193	5.746	16440756.83	
Imazamethabenz-methyl	C16 H20 N2 O3	Full match	No results	Partial mat	Full match	-0.03	288.1474	289.1546	7.013	16312266.26	
Benzocaine	C9 H11 N O2	Full match	No results	Not the top	Full match	-0.08	165.079	166.0862	6.715	15639091.61	
Pymetrozine	C10 H11 N5 O	Full match	No results	Partial mat	Full match	0.47	217.0965	259.1303	6.842	15479337.45	
(E)-Diethylstilbestrol	C18 H20 O2	Full match	No results	Not the top	Full match	0.73	268.1465	269.1538	7.563	15235927.37	
Tropicamide	C17 H20 N2 O2	Full match	No results	Full match	Full match	-0.07	284.1525	285.1597	9.728	14746157.85	
Formoterol	C19 H24 N2 O4	Full match	No results	Full match	Full match	-0.06	344.1736	343.1663	7.569	14387885.98	
Kojic-Acid	C6 H6 O4	Full match	No results	Partial mat	Full match	-0.21	142.0266	143.0339	4.112	12591968.92	
Cloprop	C9 H9 Cl O3	Full match	No results	Not the top	Full match	0.07	200.024	199.0168	4.507	12300902.42	
Amfepramone	C13 H19 N O	Full match	No results	Partial mat	Full match	-0.18	205.1466	206.1539	3.928	11899565.49	
Acephate	C4 H10 N O3 P S	Full match	No results	Not the top	Full match	-1.59	183.0116	182.0043	4.139	11448714.57	
3-Indoleacetic Acid	C10 H9 N O2	Full match	No results	Partial mat	Full match	-0.25	175.0633	208.0968	5.673	11337061.28	
Ecgonine	C9 H15 N O3	Full match	No results	Partial mat	Full match	-0.05	185.1052	186.1125	2.119	11186688.08	
Bufexamac	C12 H17 N O3	Full match	No results	Partial mat	Full match	0.13	223.1209	224.1282	2.148	10312545.16	
2,2'-Bisphenol F	C13 H12 O2	Full match	No results	Partial mat	Full match	-0.02	200.0837	199.0765	7.81	10106455.34	
Pyracarbolid	C13 H15 N O2	Full match	No results	Partial mat	Full match	-0.22	217.1102	218.1175	7.086	10015474.05	
Cloprop	C9 H9 Cl O3	Full match	No results	Not the top	Full match	-0.02	200.024	199.0167	7.665	9736869.19	
Ethoxyquin	C14 H19 N O	Full match	No results	Full match	Full match	0.12	217.1467	218.154	3.422	9583862.181	
Pyroquilon	C11 H11 N O	Full match	No results	Partial mat	Full match	-0.21	173.084	174.0913	3.838	9224795.346	
N,N'-Diphenylguanidine	C13 H13 N3	Full match	No results	Full match	Full match	0.09	211.111	212.1182	6.714	9122880.423	
Pargyline	C11 H13 N	Full match	No results	Full match	Full match	0.03	159.1048	160.1121	3.78	9046457.988	
L-Tyrosine	C9 H11 N O3	Full match	No results	Partial mat	Full match	-0.1	181.0739	180.0666	7.102	8943422.019	
Mebutamate	C10 H20 N2 O4	Full match	No results	Partial mat	Full match	0.2	232.1424	233.1496	2.137	8930120.104	
11-Hydroxy-Delta-9-Thc	C21 H30 O3	Full match	No results	Partial mat	Full match	0.33	330.2196	331.2269	11.067	8881189.528	
Buphedrine	C11 H17 N O	Full match	No results	Partial mat	Full match	0	179.131	180.1383	4.118	8166869.815	
Mescaline	C11 H17 N O3	Full match	No results	Partial mat	Full match	-0.02	211.1208	212.1281	4.043	8165358.281	
Pregabalin	C8 H17 N O2	Full match	No results	Full match	Full match	0.02	159.1259	182.1152	4.045	7724358.372	
1-Methylbenzotriazole	C7 H7 N3	Full match	No results	Not the top	Full match	0	133.064	134.0713	0.673	7463953.919	
Pyracarbolid	C13 H15 N O2	Full match	No results	Partial mat	Full match	-0.11	217.1103	218.1175	4.036	7462945.857	
Betanechol	C7 H16 N2 O2	Full match	No results	Partial mat	Full match	-0.3	160.1211	161.1284	0.688	7423879.941	
Estrendione	C18 H24 O2	Full match	No results	Partial mat	Full match	0.07	272.1777	273.1849	6.735	7283041.719	
Dibutyl Succinate	C12 H22 O4	Full match	No results	Partial mat	Full match	-0.2	230.1518	231.1591	7.055	7238652.581	
Pseudoephedrine	C10 H15 N O	Full match	Full match	Full match	Full match	0.05	165.1154	166.1227	2.271	7175792.343	54.5
4-Methyl-5-thiazoleethanol	C6 H9 N O S	Full match	No results	Full match	Full match	0.15	143.0405	144.0478	2.047	7113089.553	
Pyroquilon	C11 H11 N O	Full match	No results	Partial mat	Full match	-0.23	173.084	174.0913	4.176	6957604.935	
Buphedrone	C11 H15 N O	Full match	No results	Partial mat	Full match	-0.42	177.1153	178.1226	0.678	6840810	
Daidzein	C15 H10 O4	Full match	No results	Full match	Full match	0.1	254.0579	253.0507	6.386	6655580.211	
Spiroxamine	C18 H35 N O2	Full match	No results	Full match	Full match	-0.22	297.2667	298.274	8.437	6250267.815	
Diazinon-Oxon	C12 H21 N2 O4 P	Full match	No results	Partial mat	Full match	2.75	288.1247	289.1317	7.08	6178005.656	

Figure 32: Tentative candidates for the features selected after the filtering steps (2).



Trimethoprim	C14 H18 N4 O3	Full match	No results	Partial mat	Full match	0.37	290.138	291.1453	3.738	5923372.94	
Pyroquilon	C11 H11 N O	Full match	No results	Partial mat	Full match	-0.01	173.0841	174.0913	3.489	5803055.2	
NP-004036	C12 H22 O4	Full match	Full match	Partial mat	Full match	-0.18	230.1518	231.159	6.519	5664149.152	41.3
Alloxydim	C17 H25 N O5	Full match	No results	Partial mat	Full match	0.18	323.1733	322.1661	8.507	5642775.789	
Dinoseb	C10 H12 N2 O5	Full match	No results	Partial mat	Full match	0.08	240.0746	239.0674	7.682	5498647.536	
Spiroxamine	C18 H35 N O2	Full match	No results	Full match	Full match	0.08	297.2668	298.2741	9.132	5462389.827	
Cathinone	C9 H11 N O	Full match	No results	Not the top	Full match	-0.09	149.0841	150.0913	4.171	5446923.602	
Phenacetin	C10 H13 N O2	Full match	No results	Partial mat	Full match	0.06	179.0946	180.1019	6.794	5166022.79	
Bufexamac	C12 H17 N O3	Full match	No results	Partial mat	Full match	-0.05	223.1208	222.1136	8.274	5022646.7	
L-Methionine	C5 H11 N O2 S	Full match	No results	Partial mat	Full match	0.08	149.0511	150.0584	1.243	4965589.603	
Dibutyl Succinate	C12 H22 O4	Full match	No results	Partial mat	Full match	0.14	230.1518	231.1591	8.366	4905764.967	
Cathinone	C9 H11 N O	Full match	No results	Not the top	Full match	0.19	149.0841	150.0914	3.083	4746210.706	
Hippuric Acid	C9 H9 N O3	Full match	No results	Partial mat	Full match	-0.34	179.0582	180.0655	2.252	4254145.976	
Harmine	C13 H12 N2 O	Full match	No results	Full match	Full match	0.27	212.095	213.1023	6.335	4213578.208	
Buphedrine	C11 H17 N O	Full match	No results	Partial mat	Full match	-0.17	179.131	180.1383	8.095	4145037.252	
Prolintane	C15 H23 N	Full match	No results	Partial mat	Full match	-0.07	217.183	218.1903	4.733	4023843.228	
Pyrinuron	C13 H12 N4 O3	Full match	No results	Partial mat	Full match	-2.07	272.0904	271.0831	5.676	3914830.79	
Nabumetone	C15 H16 O2	Full match	No results	Partial mat	Full match	-0.42	228.1149	229.1222	6.637	3441013.605	
Edrophonium	C10 H15 N O	Full match	No results	Partial mat	Full match	-0.09	165.1154	166.1226	7.584	1966486.796	

Figure 33: Tentative candidates for the features selected after the filtering steps (3).

G.2 Target compounds

Table 26: List of target compounds in LC-HRMS analysis of sediment and soil extracts. Most of them are swiss-specific micropollutants from municipal wastewater.

Compound	$\log K_{ow}$	Use	STDI
6PPD	5,40	antioxidant in rubber tire	6PPDQ d5
6PPDQ	3,96	subproduct of 6PPD	6PPDQ d5
Amisulpride	1,10	neuroleptic+antidepressant	Amisulpride-d5
Benzotriazole	1,23	corrosion preventative	Benzotriazole-d4
BT	2,01	food additive, source of derivatives	BT d4
Candesartan	4,79	antihypertensive	Candesartan-d5
Carbamazepine	2,45	Anticonvulsant	Carbamazepin-d10
Citalopram	3,50	antidepressant	Citalopram-d6 HBR
Clarithromycin	3,16	antibiotic (angina)	Clarithromycin-d3
Diazinon	3,30	pesticide/insecticide organophos.	Diazinon d10
Diclofenac	4,51	anti-inflammatory	Diclofenac-d4
DPG	2,89	rubber vulcanization accelerator	DPU d10
HBT	1,76	tire additive derivative	BT-d4
Hydrochlorothiazide	-0,07	diuretic	Hydrochlorothiazide-C13,d2
Irbesartan	5,31	antihypertensive	Irbesartan-d6
MBT	2,42	rubber vulcanization accelerator	BT-d4
Methylbenzotriazole	1,89	corrosion preventative	Methylbenzotriazole -d6
Metolachlor	3,00	pesticide/ herbicide	Metolachlor d6
Metoprolol	1,88	beta blocker	Metoprolol-d7
Progesterone	3,87	hormone	Progesterone-2,3,4-13C3
Propiconazole	3,88	biocide/ fongicide	Propiconazole d5
Testosterone	3,32	hormone	Progesterone-2,3,4-13C3
Venlafaxine	2,80	antidepressant	Venlafaxin-d6
Metformine	-1,43	diabetes treatment	Metformin d6
17a-Estradiol	4,10	natural estrogens	17b-estradiol d3
17b-Estradiol	4,10	natural estrogens	17b-estradiol d3
Bisphenol A	3,32	additive	Bisphenol A d6
Chlorpyrifos (ethyl)	5,00	pesticide/insecticide organophos.	Chlorpyrifos methyl d6

Recovery of test sample

A recovery test was conducted by extracting with ASE triplicates of the sediment sample MB2, spiked with 25 μL of a mix of 23 internal standards at $\pm 1 ng/mL$. A method blank, obtained by following the same ASE protocol but without the addition of a sample, was realised. Extracts of sample MB2 gave suitable recoveries for most internal standards, with an overall mean of $53 \pm 35\%$ (see figure 35). Metformin d6 (0.00 %), Methybenzothriazole d6 (15 ± 1%), Benzotriazole d4 (12 ± 2%), Diclofenac d4 (0.00 %)and Candesartan d5 (0.11 ± 0.06%) gave bad results. Nevertheless, other compounds with similar polarity had higher recoveries rate, meaning that other factors are influencing their extraction. All other compounds (16 in total) had recovery values at least above 30 %, with 8 compounds' recoveries being higher than 70 %. The results of the recovery test suggest that organic compounds with a broad range of polarities can be extracted by the chosen ASE method. Therefore, the protocol was applied to every sample in order to quantify the target compounds (see list table

26) and to proceed to non-target screening.

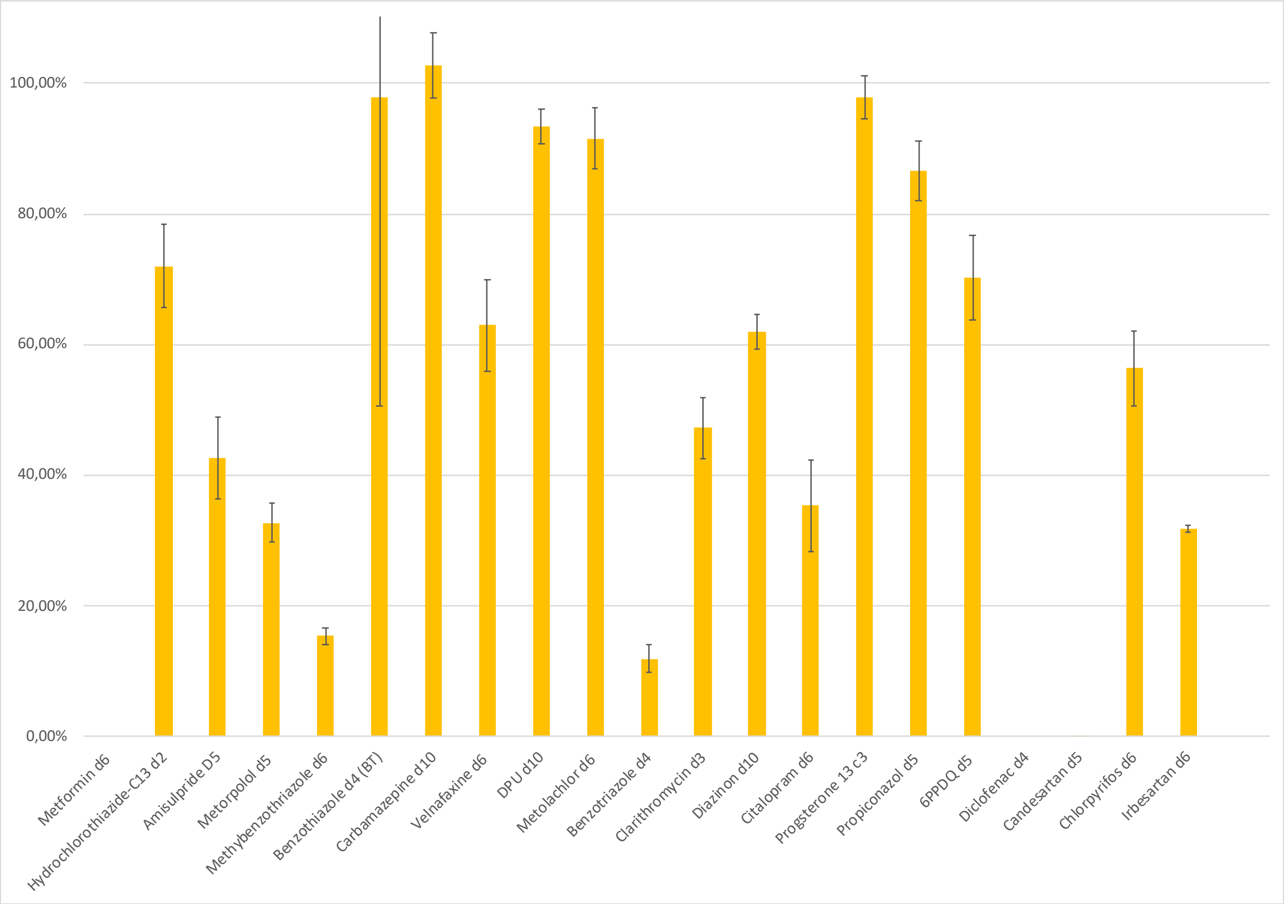


Figure 34: ISTD recoveries in ASE extract from test sample (sediment MB2 spiked with 25 μL of the mix of ISTD). *The barplot values are the mean recoveries ± standard deviation (represented by error bars) of the triplicates. ISTD are ranked from lowest (-1.43) to highest (5.31)* $\log K_{ow}$.

Recoveries of sediment and soil sample

The following Figure shows the mean ISTD recoveries of all soil and sediment samples. The overall recovery mean of 34 ± 22% is lower than the recovery obtained for the test sample. The same compounds presented were not or badly extracted by the ASE method: Metformin d6 (0.23 ± 0.22 %), Methybenzothriazole d6 (11.39 ± 6.31%), Benzotriazole d4 (11.91 ± 5.34%), Diclofenac d4 (0.57 ± 0.36 %)and Candesartan d5 (0.89 ± 0.55%). Moreover Amisulpride D5, chlorpyrifos d6, Clarithromycin d3, irbesartan d, metorpolol d5 had recoveries below 30 %. All other compounds (11 in total) had recoveries above 30 % and 7 above 50%.

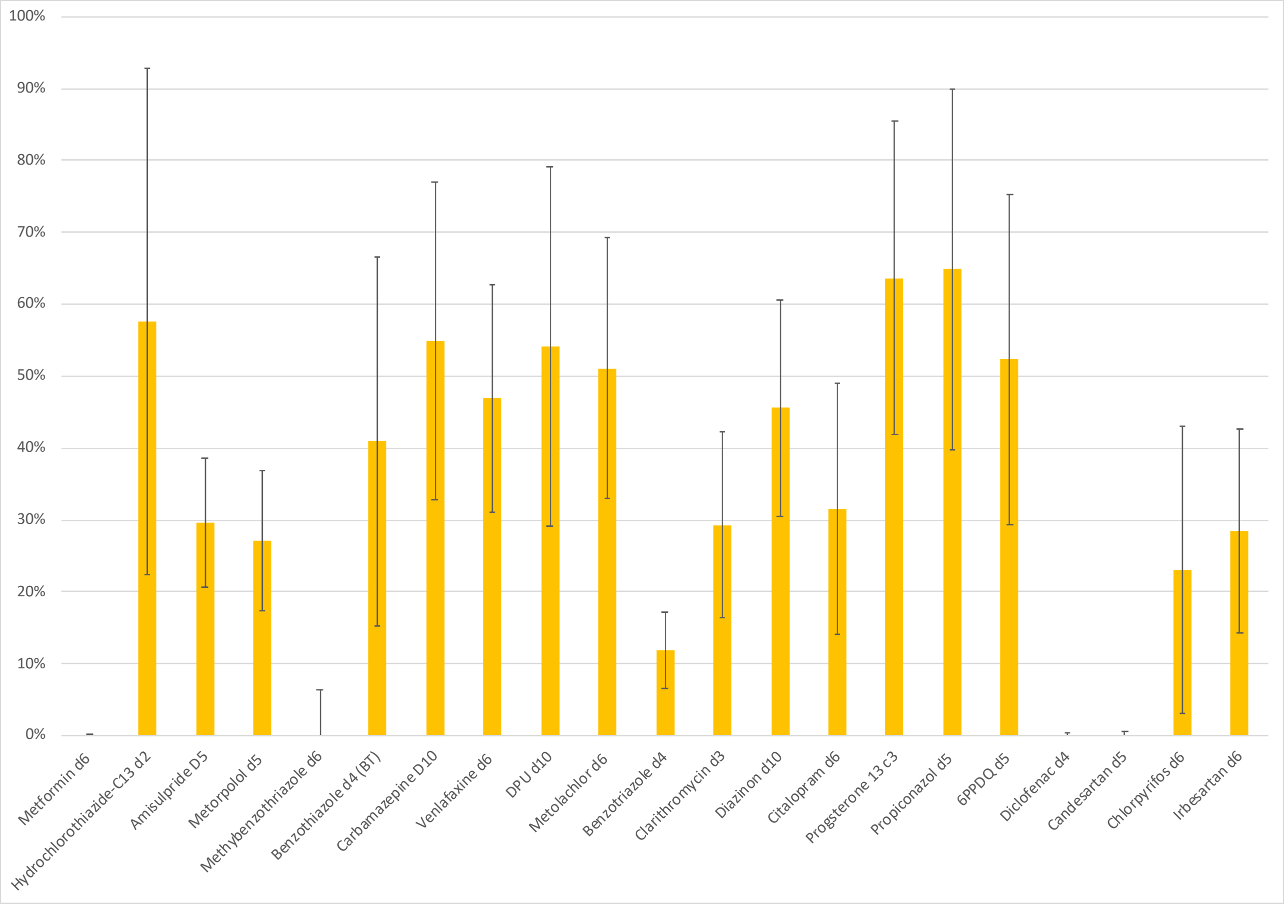


Figure 35: Mean ISTD recoveries in ASE extract from triplicates of soil and sediment sample spiked with 25 μL of the mix of ISTD. *The barplot values are the mean recoveries* ± *standard deviation (represented by error bars) ISTD are ranked from lowest (-1.43) to highest (5.31)* $\log K_{ow}$.

H Statistical data analysis

Hierarichical clustering

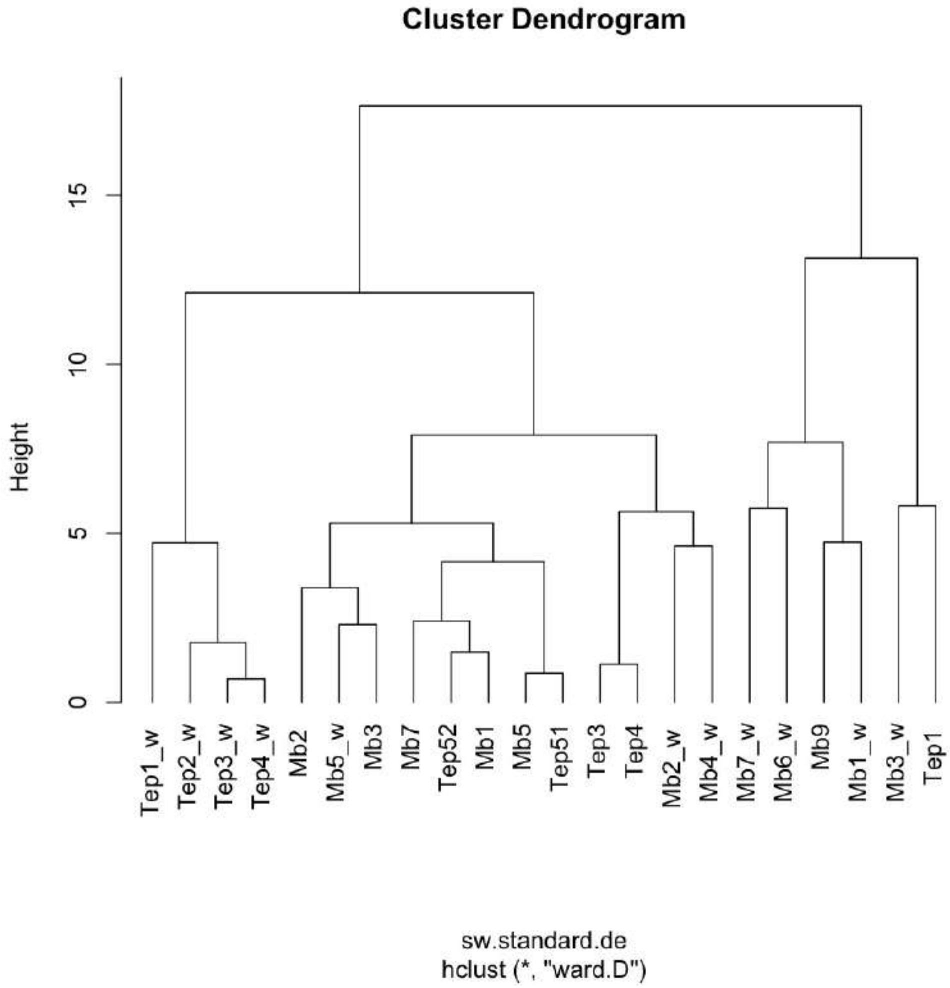


Figure 36: Dendogram obtained by hierarchical clustering (ward method on gower distance matrix) of physio-chemical parameters, heavy metals, HAPs and PCBs.

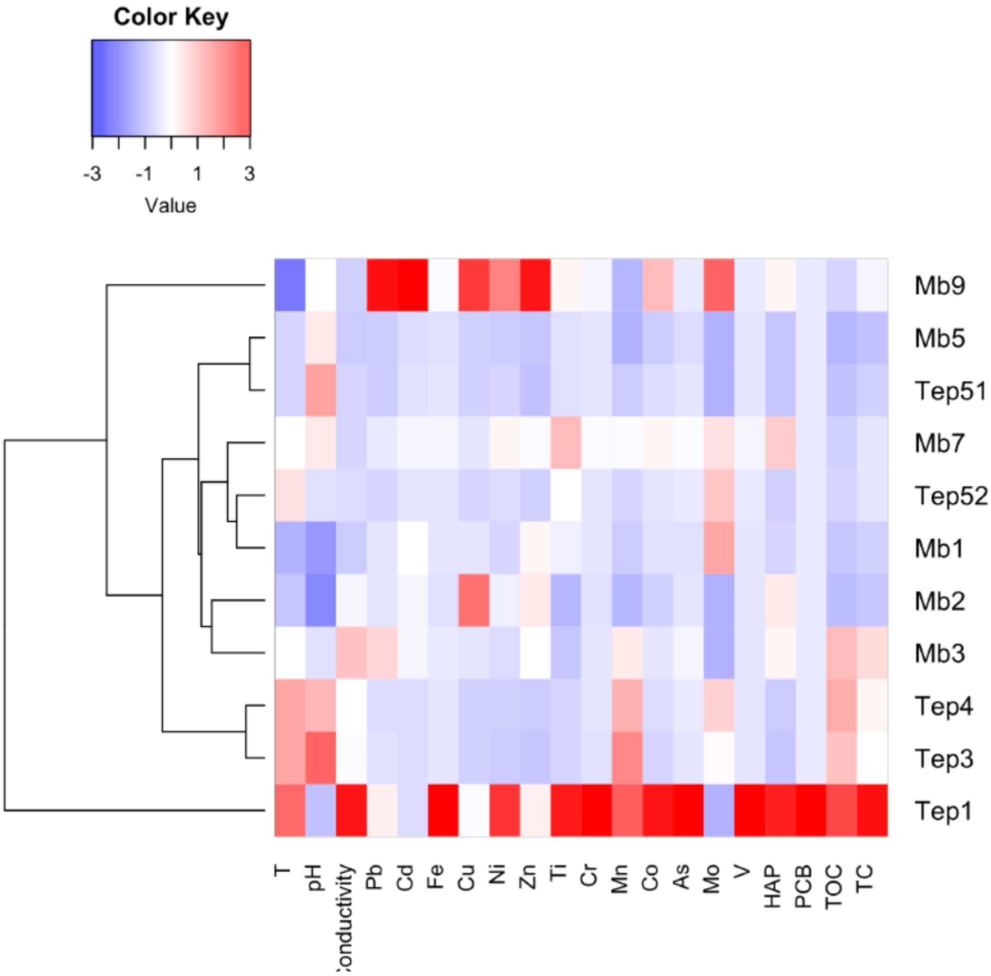


Figure 37: Heatmap and dendogram obtained by hierarchical clustering for soil/sediment samples with physicochemical parameters, heavy metals, HAPs and PCBs.

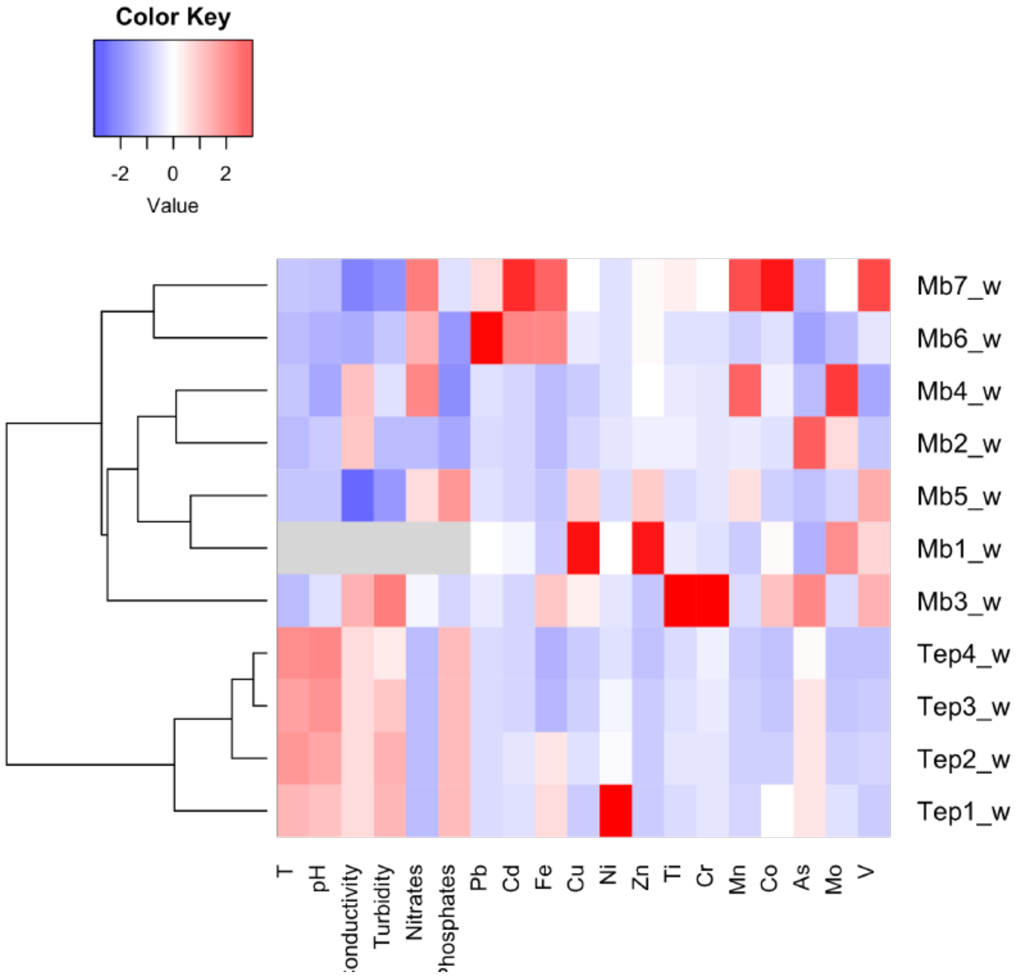


Figure 38: Heatmap and dendogram obtained by hierarchical clustering for water samples with physicochemical parameters and heavy metals.

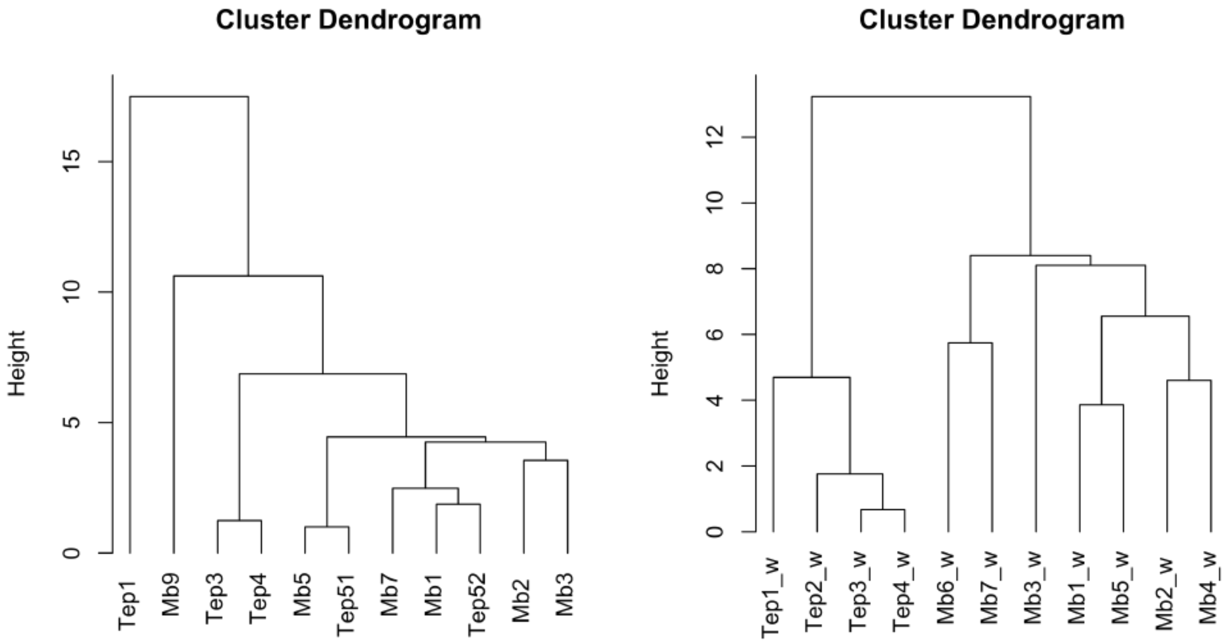


Figure 39: Hierarchical clustering based only on metal data from soil/sediment and from water samples.

Principal component analysis

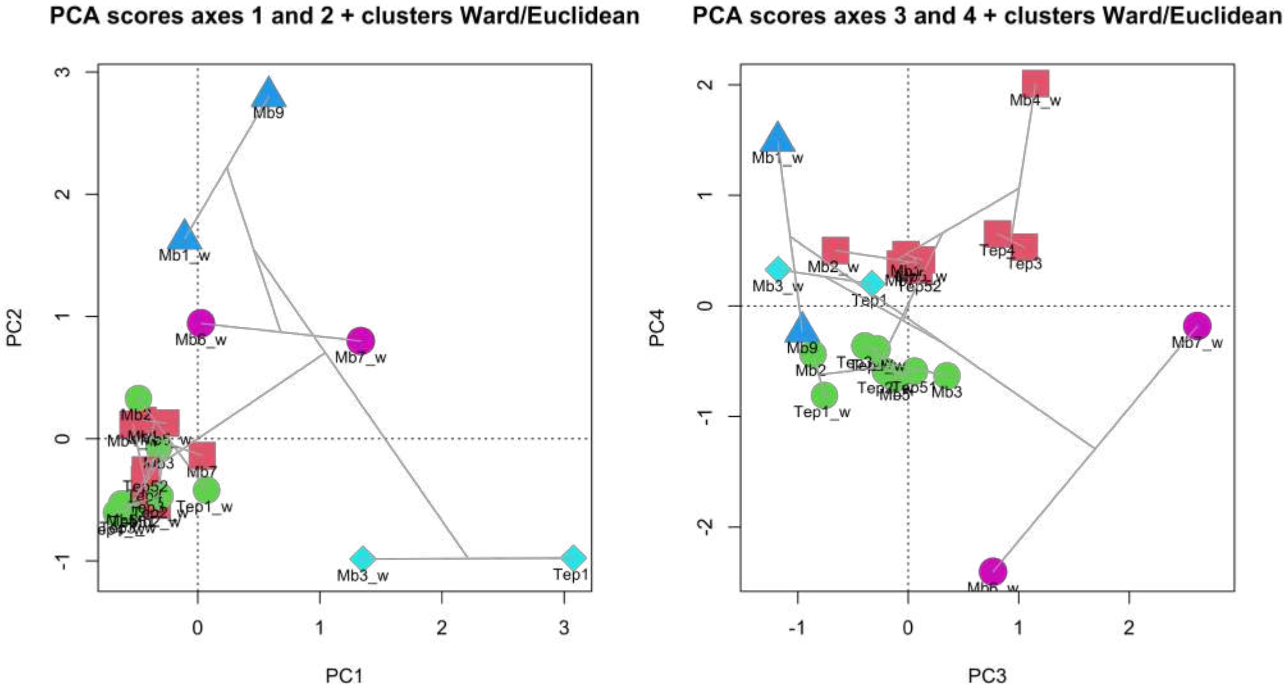


Figure 40: Principal components analysis (based on metal data) and groups obtained from the clustering (based on all data) for soil/sediment and water samples.

According to Kaiser's rule we should interpret the results along axis PC1/PC2/PC3/PC4 whereas the brocken stick model recommend to interprete only PC1/PC2 (see Figure 41). The percentage of variance explained by each axis is as follow:

- Axis 1: 38 %
- Axis 2: 25%
- Axis 3: 11%
- Axis 4: 9%

The interpretation of PC3 and PC4 is thus debatable given their much lower contribution to overall data variance.

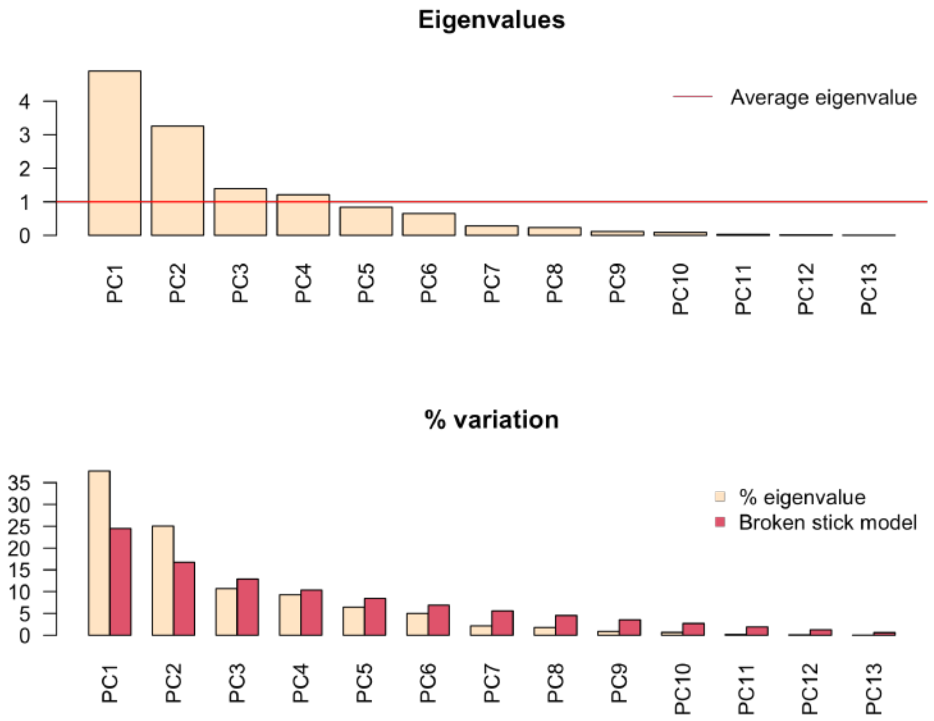


Figure 41: Kaiser's rule and brocken stick model for the selection of the number of interpretable PCA axes.

The following Figures present the PCA for water and soil/sediment samples separately.

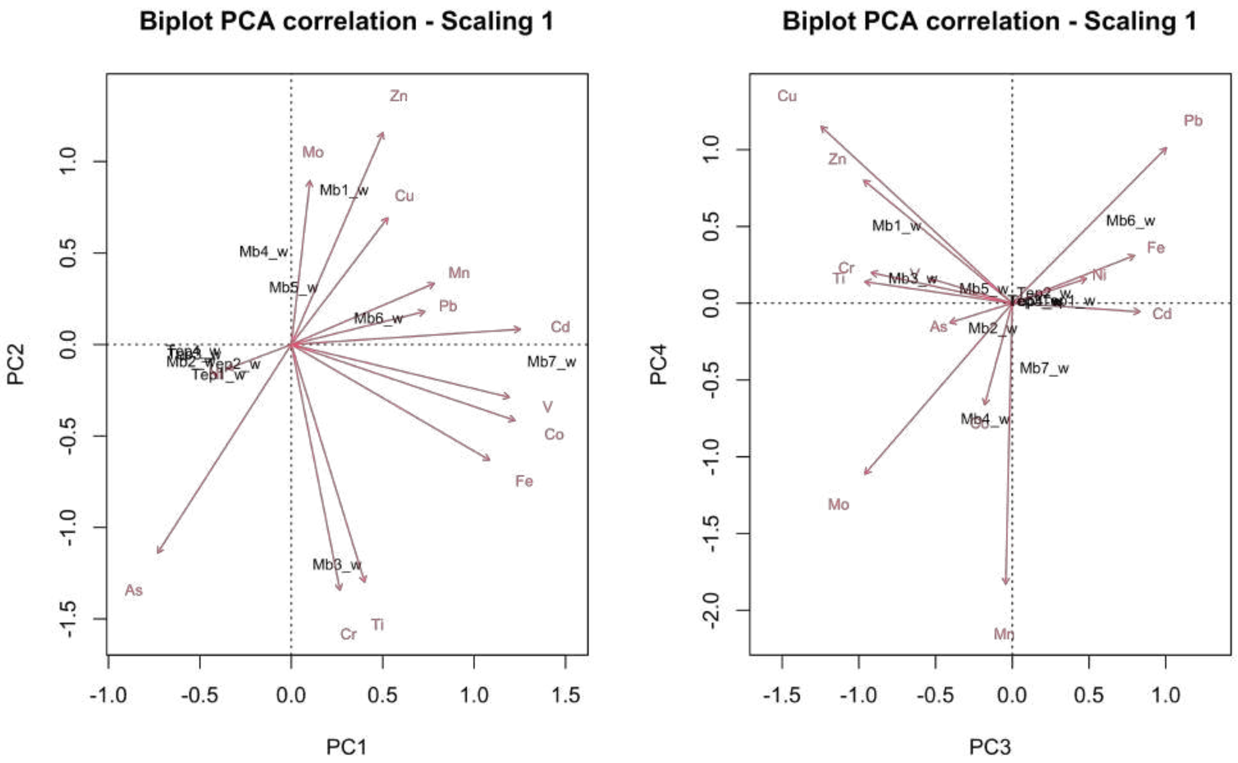


Figure 42: Principal components analysis only on metal data from water samples (other variables have missing values). Percentage of variance for each axis is 31 % (PC1), 23% (PC2), 17% (PC3), 12% (PC4). The four axis are interpretable according to Kaiser's rule and the brocken stick model.

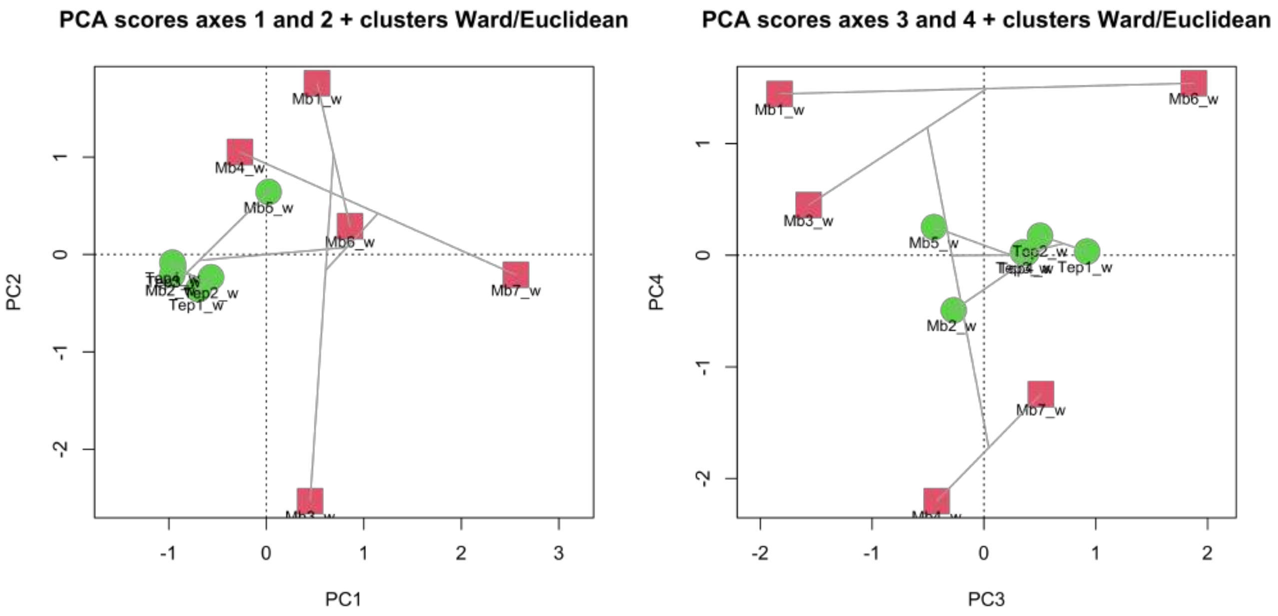


Figure 43: Hierarchical clustering based on all variables and PCA only on metal data from water samples. Percentage of variance for each axis is 31 % (PC1), 23% (PC2), 17% (PC3), 12% (PC4). The four axis are interpretable.

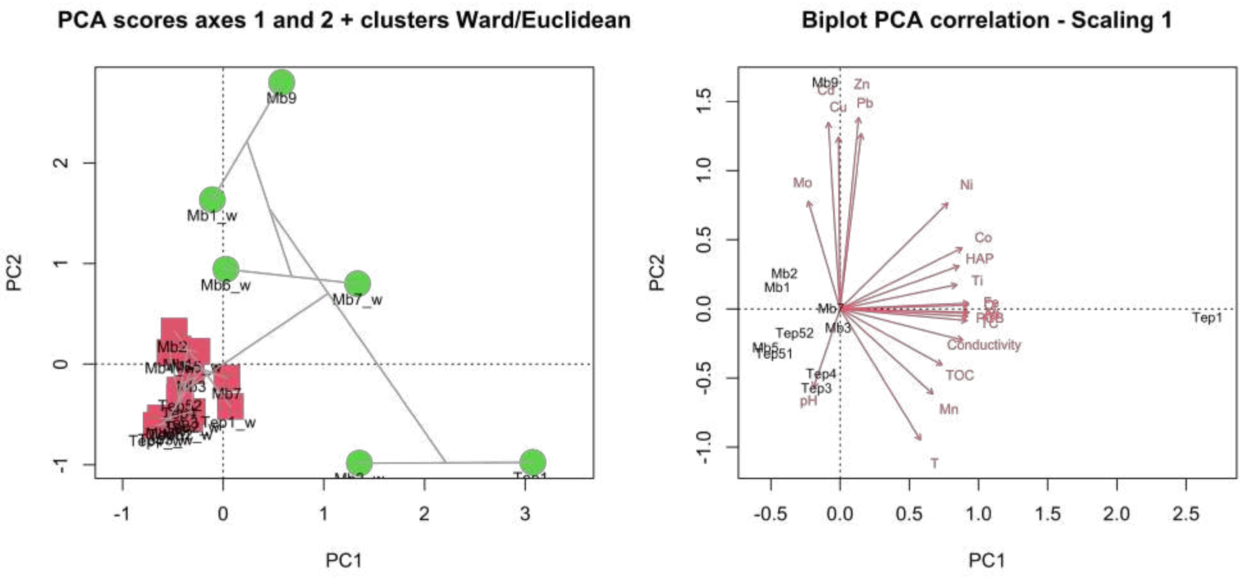


Figure 44: Hierarchical clustering based on all variables and principal components analysis on metal data, PAHs, PCBs and physicochemical data from soil/sediment samples. Percentage of variance for each axis is 58 % (PC1), 25% (PC2). Only the first axis two are interpretable.

Statistical tests

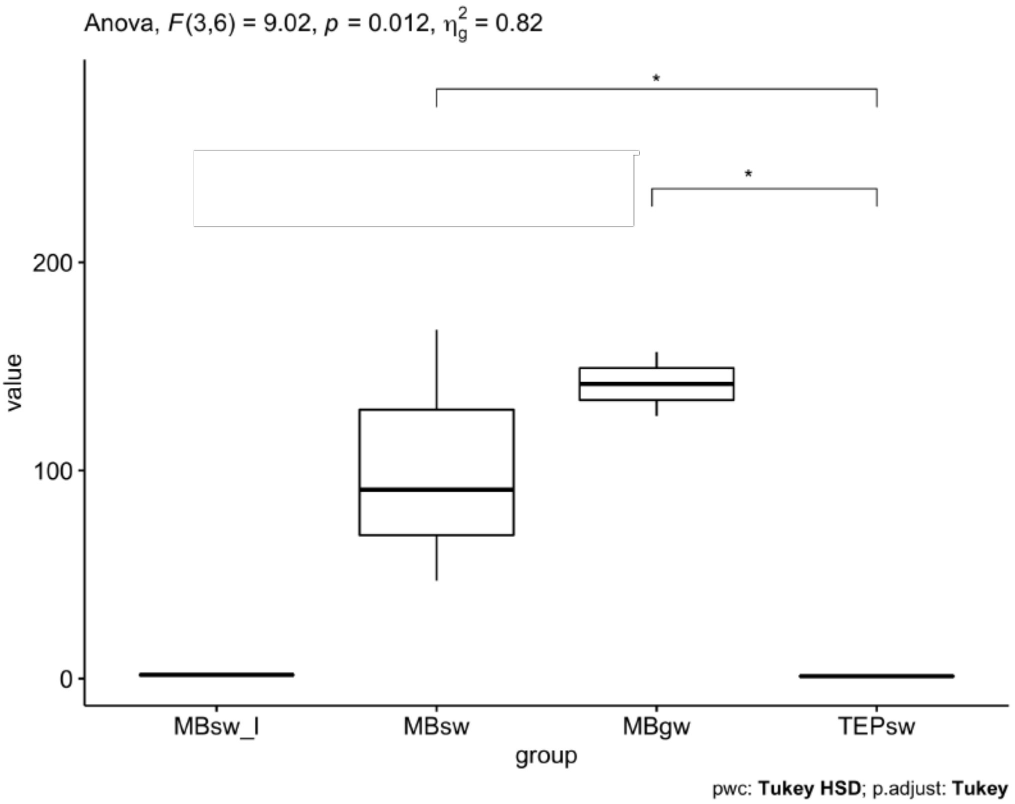


Figure 45: Boxplots of nitrate concentration in superficial water from ponds ($MBsw$), lake ($MBsw_l$), groundwater ($MBgw$) of Mbeubeuss and superficial water from Technopole ($TEPsw$) with the result of ANOVA test and Tukey's test (*p-value* <0.05 represented by a star).