JOINT COOPERATION PROGRAMME
BANGLADESH – THE NETHERLANDS

Technical Report 7

Innovative monitoring and monitoring strategy for hazardous pollutants

Urban Water Quality Management for Dhaka City

JCP Technical Report 7

Innovative monitoring and monitoring strategy for hazardous pollutants Urban Water Quality Management for Dhaka City

October 2022

Developing the partnership for applied research by

Deltares CEGIS Center for Environmental and Geographic Information Services WAGENINGEN UNIVERSITY & RESEARCH IWM Water Environment & Climate Kingdom of the Netherlands

Joint Cooperation Programme Bangladesh Netherlands
Knowledge development for a prosperous delta

Document information

Document Title	Innovative monitoring and monitoring strategy for hazardous pollutants
Author(s)	Hans Aalderink, Jasperien de Weert, Daniel Giesen, Abdur Rahman, Rianne van den Meiracker.
Reference	

Dissemination level

- ☑ Technical Report
- ☐ Technical Note
- ☐ Planning and Progress Report
- ☐ Others

Dissemination level

- ☑ Public
- ☐ Other Programme Partners
- ☐ Restricted to a specific group
- ☐ Confidential

Document Version and Review Management

Version No.	*Status*	*Date*	*Author(s)*	*Review*	*Approval*
1	Drat	04-11-2022	Hans Aalderink	Johan Valstra	WO
2					
3					

Key Project Information

This document is an output of the Joint Cooperation Programme (JCP) Bangladesh – the Netherlands

Grant agreement No.	DHA/OS/2018/4000001952
Grant organization	Embassy of the Kingdom of the Netherlands (EKN)
Project manager	William Oliemans
Project start date	December 2018
Project duration	4 years
Coordinating organization	Stichting Deltares
Partner organization	Center for Environmental and Geographic Information Services (CEGIS), Institute of Water Modeling (IWM), Wageningen University and Research (WUR).

SUMMARY AND CONCLUSIONS

This technical note is one of the results of the Pillar I Work Package 3: "Urban Water Quality Management for Dhaka City- "Clean and Safe Water for Dhaka City". This project included the following activities:

1. Innovative monitoring and monitoring strategy for hazardous pollutants;
2. Development of an integrated information platform for water quality and pollution sources;
3. Development of tools for modelling of pollution loads and water quality impacts;
4. Development of a transition strategy for water pollution control.

This note describes the outcomes of activity 1. The activity aims to provide a sound knowledge base for the authorities concerned to develop an integrated monitoring strategy for hazardous pollutants. Goal is to investigate the options for implementation of cost-effective routine monitoring of emerging compound in Bangladesh and to make an operational plan for monitoring. Therefor we explored the application passive sampling as an innovative method to monitor these types of hazardous pollutants.

Samples were taken at 10 locations in the rivers using passive sampling. The locations were chosen on the basis of possible hotspots of sources of pollution. Samples were taken during the monsoon and the dry season. The samples were analyzed in Bangladesh by Plasma Plus, a laboratory affiliated with the Independent University of Bangladesh (IUB). The intention was to analyze the samples for a wide range of contaminants. However, due to the availability of the required standards, it was possible to test samples for PCBs and OCPs. Another limitation was the limited accuracy of the analysis equipment used, which made it impossible to calculate adsorbed amounts of contaminants back to concentrations in the water. The results therefore only provide insight into the occurrence of the measured substances. The results show that many of the investigated substances have been found in the water. This also applies to the OCP's, the use of which has been banned under the Stockholm Convention. Bangladesh has signed this convention and has taken measures to prevent its use. Other project-based research also shows that contamination with pesticides and pharmaceuticals is a major problem.

This shows the importance of routine monitoring networks. To perform measurement programs on a large scale, requires a laboratory that is specialized in performing such analyses. A laboratory that is able to do the analysis on a routine base, should be equipped with GC-ECD, GC-MS and having sufficient equipment and chemicals for sample preparation and analysis. In particular high-quality standard should be available to allow for the determination of a broad spectrum of emerging pollutants. Hence significant investments in facilities, equipment and supplies as well as human resources are required, requiring a significant period of catalytic support from development partners, to upgrade the capacity, and make it operational. This effort, however, needs to be accompanied by improving the legislative framework and providing sufficient public funding to maintain operational surveillance and monitoring activities. The DoE, being responsible for water quality is the most appropriate organization to carry out these measurement programs.

Passive sampling was used in this study. This is a cost-effective sampling method. Because time-averaged concentrations are measured with this method, a representative picture of the contaminant can be obtained with a lower sampling frequency. It should be noted that according to many international guidelines for the sampling of emerging compounds, grab sampling is used. Passive sampling is becoming more and more common internationally and there is discussion about including the use of passive sampling in the regulations.

TABLE OF CONTENTS

ACRONYMS AND ABBREVIATIONS

BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DAE	Department of Agricultural Extension
DoE	Department of Environment
DoF	Department of Fisheries
DPHE	Department of Public Health Engineering
DWASA	Dhaka Water Supply and Sewerage Authority
ERD	Economic Relation Division
GC-ECD	Gas chromatography- electron capture detector
GC-MS	Gas chromatography–mass spectrometry
HCH	Hexachlorocyclohexane
IUB	Independent University of Bangladesh
MoEFF&C	Ministry of Environment Forestry & Climate Change
OCPs	Organochlorine Pesticides
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PFAS	Per and Poly Fluoroalkyl Substances
POPs	Persistent Organic Pollutants
PRCs	Performance Reference Compounds
WARPO	Water Resources Planning Organization

LIST OF TABLES

LIST OF FIGURES

1 INTRODUCTION

There is a long tradition for routine monitoring of water quality in Bangladesh. For example, the Department of Environment collects data on a routine basis on parameters (such as BOD, COD, Nutrients, bacteria and to a certain extent also on heavy metals). Also, DWASA and DoF, DPHE, WARPO and DAE collect water quality data. These monitoring networks provide useful information about the state of the rivers and to identify hotspots of pollution and trends.

What is missing is information about other contaminants such as pesticides, and other so-called emerging compounds. Emerging pollutants are chemicals and compounds that have recently been identified as dangerous to the environment, and consequently to the health of human beings. These pollutants include a variety of compounds such as antibiotics, pharmaceuticals, steroids, endocrine disruptors, hormones, industrial additives, chemicals. Municipal, industrial, and domestic wastewater are the primary pathway for their wide diffusion in the aquatic environment. It is widely acknowledged that these emerging pollutants are increasingly becoming a hazard.

For example, in Europe and the USA there is nowadays much attention on PFAS (per and poly fluoroalkyl substances). These are widely used, long lasting chemicals, components that break down very slowly over time and maybe linked to harmful health effects in humans and animals.

Monitoring of this type of pollutants in Bangladesh is sometimes done on a project base and in scientific studies, but there is no routine monitoring for these compounds. However, it is important to keep an eye on things and to recognize these new problems in time, so that appropriate measures can be taken. It should be realized that traditional treatment methods do not remove all these pollutants. That could have consequences for the design of wastewater treatment plants and drinking water treatment plants. To be prepared to the future more advanced technologies will be needed.

Routine monitoring for these pollutants is a challenge:

- Laboratory analysis is not straight forward. It required specialized equipment
- Cost for analysis are high (up to US$ 10,000, - per sample)
- Concentrations are often low and that require advanced analytical method.
- The variation in concentration is high, which makes representative sampling not easy.

The project aims to provide a sound knowledge base for the authorities concerned to develop an integrated monitoring strategy for hazardous pollutants. Goal of this project is to investigate the options for implementation of cost-effective routine monitoring of emerging compound in Bangladesh and to make an operational plan for monitoring. Therefor we explored the application passive sampling as an innovative method to monitor these types of hazardous pollutants.

2 THE USE OF PASSIVE SAMPLING

Water quality monitoring normally occurs by grab sampling several litres of water, sending them to the lab and extracting and analysing immediately. This way of sampling gives a snapshot of the water quality at the moment of sampling. Especially with substances that have an irregular emission pattern, like pesticides, peak concentrations will easily be missed. And because of the limited sampling volume, often concentrations are below the limits of detection and little information on the water quality is obtained. Water quality monitoring of substances can also be performed with passive sampling.

Passive sampling is a technique at which a sampler with sorption material is exposed to water. They are applied in seas, lakes, ditches and even in groundwater wells for periods that can vary from several weeks to months. During the exposure, substances are sampled by diffusion from a large volume, generally resulting in lower detection limits when compared to classical grab sampling. The result is a time integrated average concentration that includes peaks in the concentrations. This gives more valuable information on the substances that were present in the water (See Figure 1)

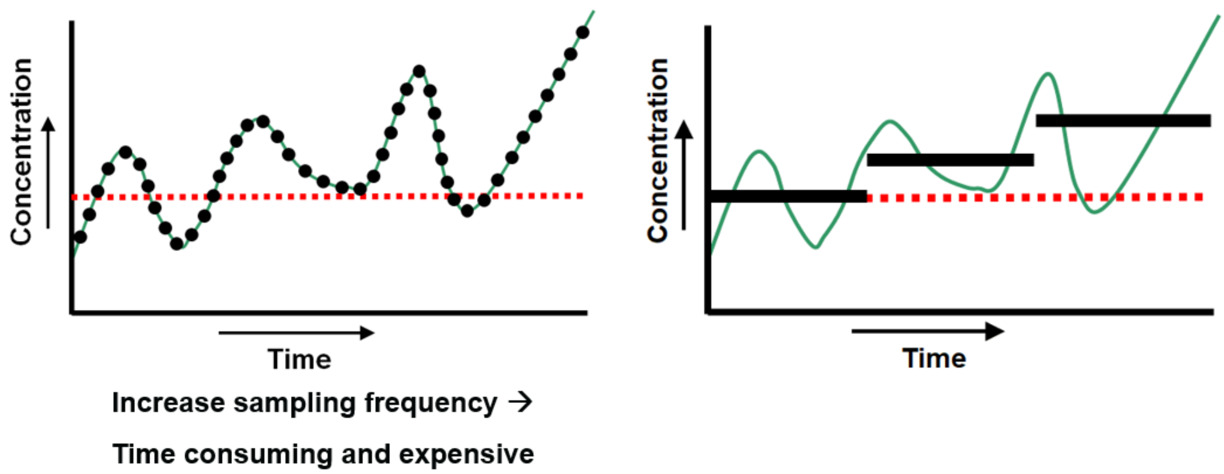


Figure 1 Time averaged sampling using passive samplers

A further benefit is that the passive samplers do not need to be extracted immediately after a sampling period. Samplers from different sampling periods can be collected, stored in a simple freezer and easily sent to a laboratory for extraction and analysis. This is especially beneficial for worldwide water quality monitoring and in remote areas with limited analytical infrastructure and where transport of water samples is problematic.

There are different types of passive samplers (see Figure 2). What sampler is useful for certain monitoring depends on the substances that will be monitored. For hydrophobic substances, silicone rubber is an ideal material. It consists of a small sheet of silicone rubber, is easy to deploy and very robust. It has been widely used for marine sampling on rough seas, but it has also proved to work well in rivers and ditches. The uptake mechanism is well understood and with known partition coefficients and an adsorption model, the amount of substances found on the sampler can be converted to the average water concentration during the monitoring period.

For hydrophilic/polar substances, Speedisk samplers can be used. This consists of a hard propylene cage with adsorption material and a glass fibre filter to keep the sorption material in the sampler. Speedisks are already regularly used in laboratories to extract water samples. By using them as a passive sampler, the extraction takes place in the field and the laboratory procedure also used for classical water samples can be followed for subsequent extraction of the sampler. That makes it an easy tool to apply. When the Speedisk is applied in combination with silicone rubber samplers, an indicative / semi quantitative aqueous concentration can be derived. Recent studies showed that both silicone rubber and speedisk samplers detect many more substances compared to grab samples taken in the same period. This was mainly due to lower detection limits, but also to peak concentrations in the water that were missed by the grab samples. The resulting time averaged concentrations gave better information on the water quality and makes it possible to follow trends in water quality.

Figure 2 Types of passive samplers (Silicon rubbers left picture and Speedisk sampler right picture)

3 MONITORING

The use of passive samplers has been tested in the rivers in and around Dhaka. All these rivers have been recognized as heavy polluted, receiving untreated domestic and industrial wastewater. The following rivers have been included in the monitoring:

- Buriganga River
- Shitalakhya River
- Turag River
- Balu River

Selection of the sampling locations was based on a hotspot analysis.

3.1 Water Pollution Hotspot analysis

The water pollution hotspots have been identified based on pollution sources such as point source (industrial pollution) and non-point source (agricultural run-off, sediment pollution from riverbank erosion, urban runoff and others). The geospatial technique for Optimized Hotspot Analysis is followed to prepare the hotspot maps for point source pollution and Landsat Enhanced Thematic Mapper 8 Satellite images are used to prepare non-point water pollution map. Watersheds are delineated using the SWAT Model in ArcGIS. For each river basins such a hotspot analysis has been made. The results are presented in the figures below.

In order to connect as much as possible to the existing DoE monitoring network, these monitoring locations were also included in the final selection of sampling locations.

Tentative Strategic Location Map:Buriganga River

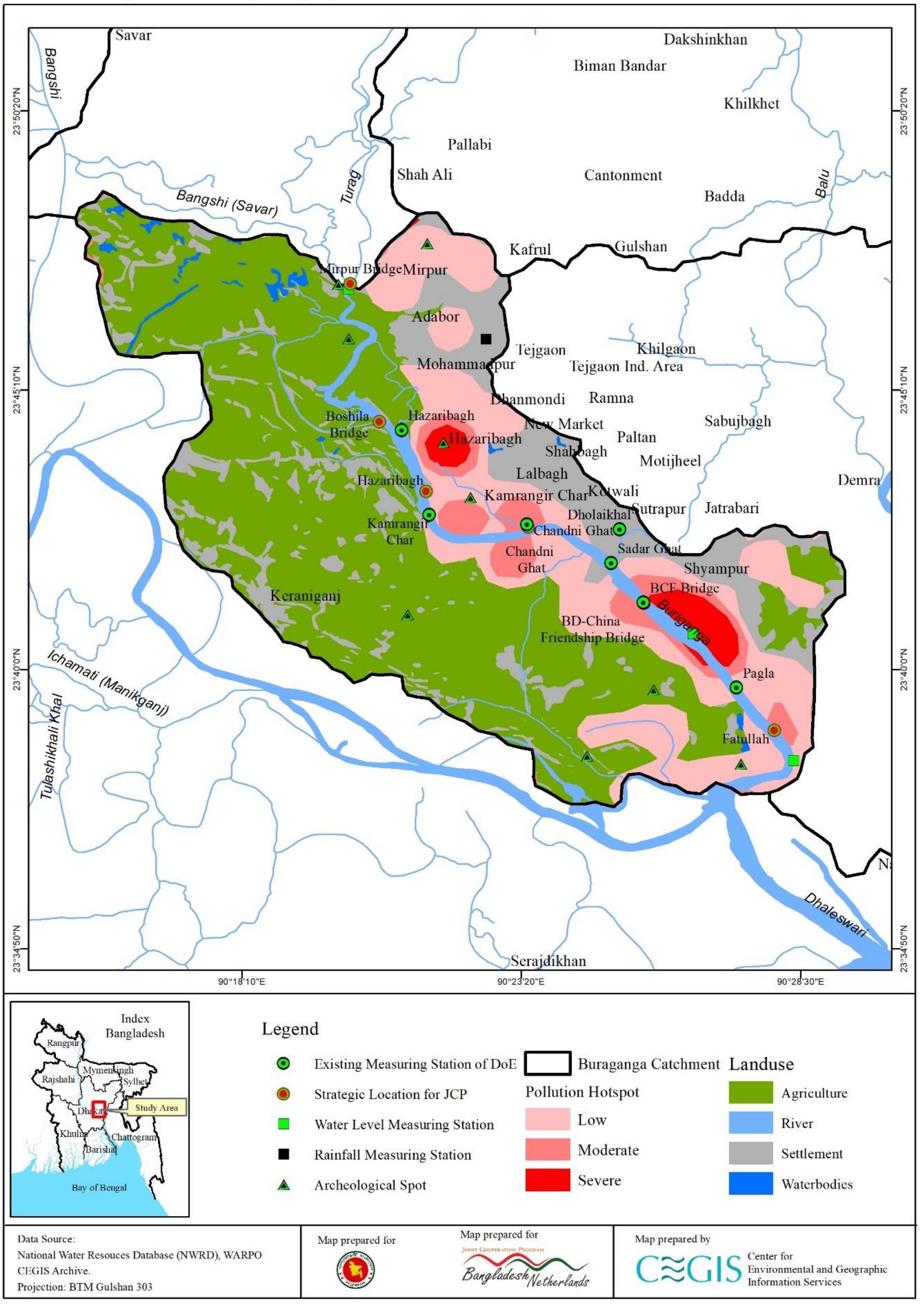


Figure 3 Pollution hotspots for Buriganga River

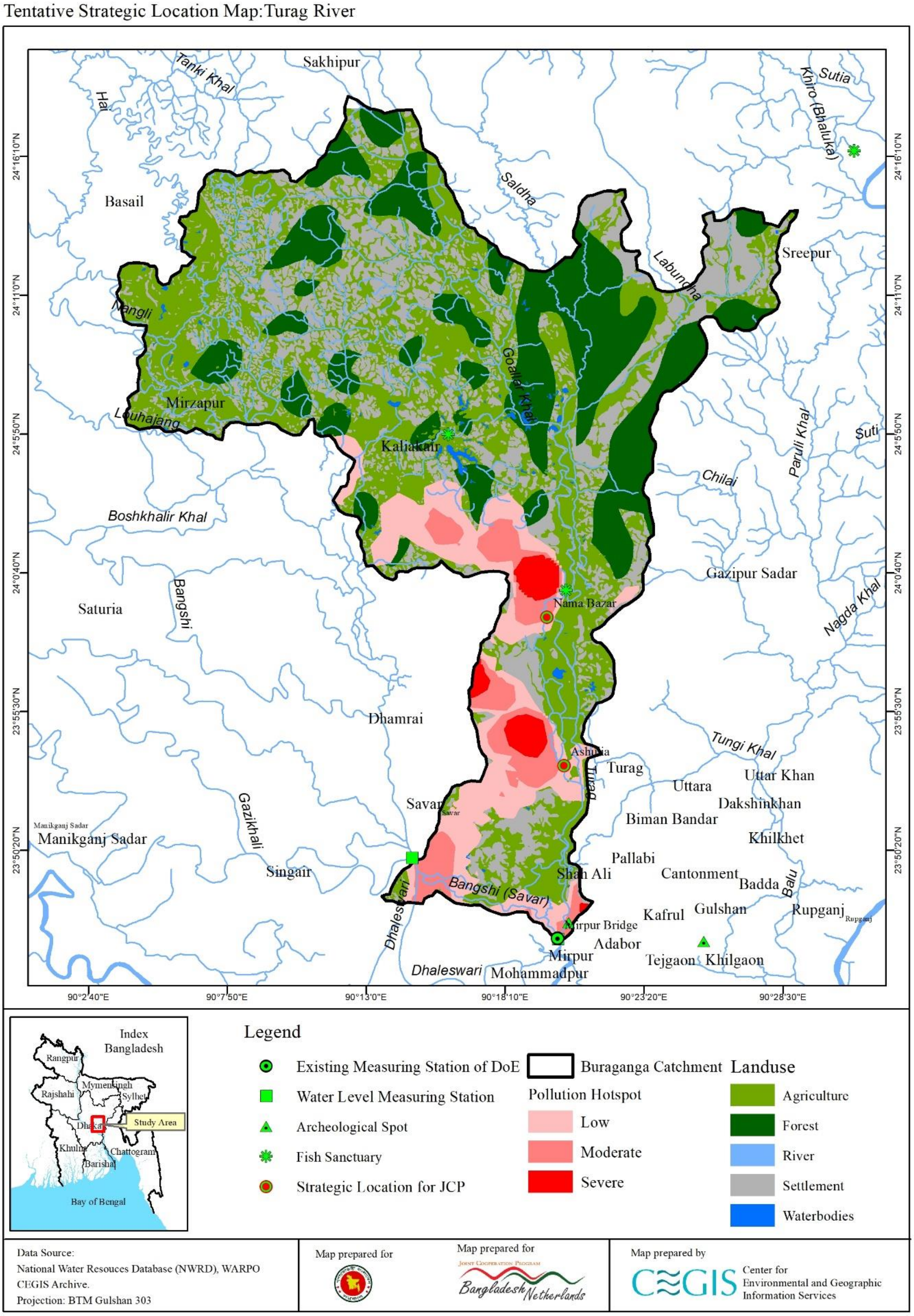


Figure 4 Pollution hotspots for Turag River

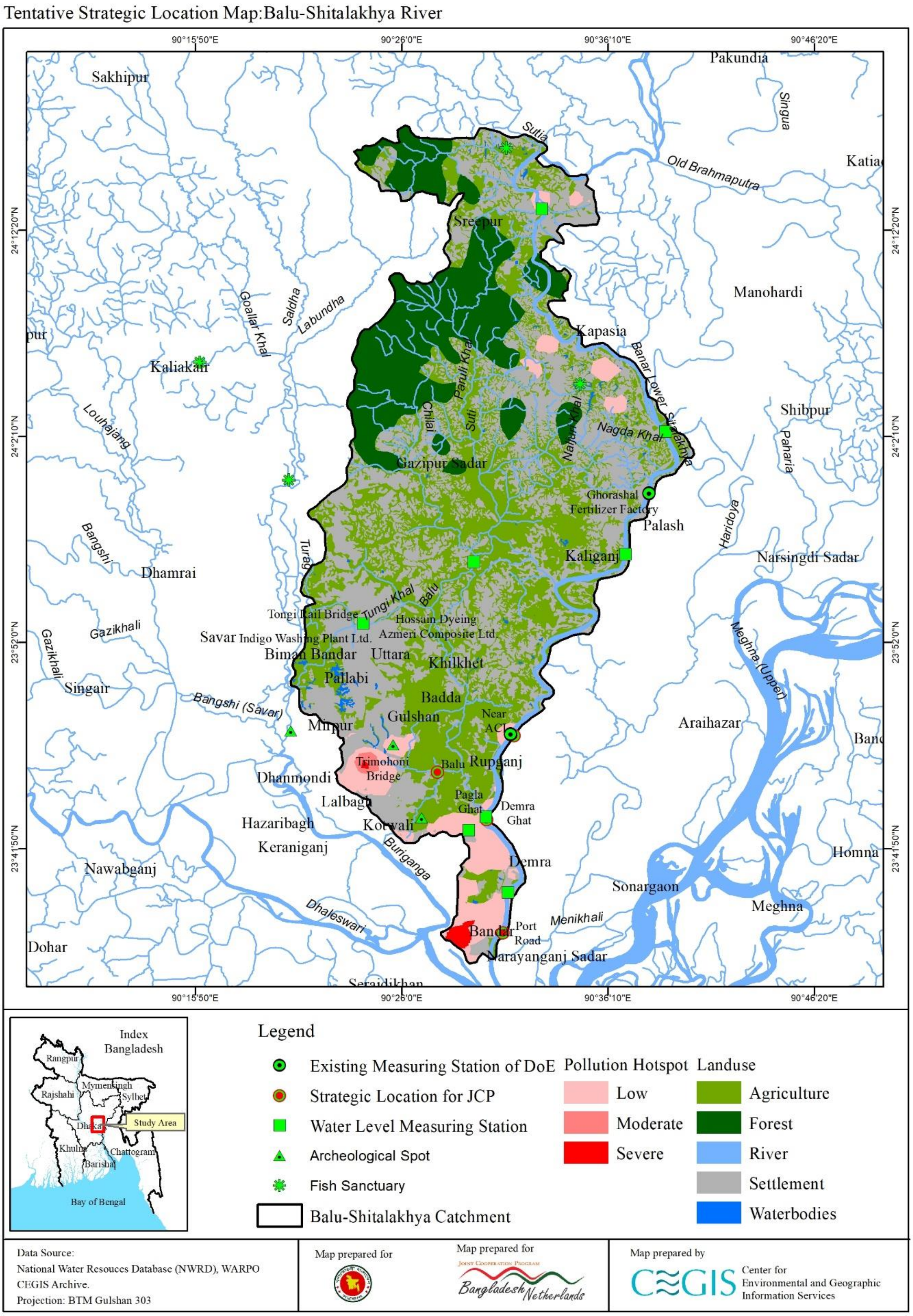


Figure 5 Pollution hotspots for Balu and Shitalakhya River

3.2 Selected sampling locations

A set of criteria have been followed to further identify the final strategic locations which include the following:

- Location of the river with major environmental sensitive receptors (social forestry, community park, water bodies, nearby agricultural land and so on);
- Population density and habitat;
- An area with local association of water pollution phenomenon between observation and its neighbour;
- Current use of river water e.g., drinking, agricultural, fish culture and other purposes;
- Pollution hotspots around the strategic locations;
- Industrial dense zone;
- Areas near archaeological & historically significant sites;
- Drainage outfalls into the rivers;
- Rivers used as industrial effluent discharge outfalls;
- Areas with good transport/communication facilities;
- Physical characteristics of the river area, such as tributary, distributary, and confluence of rivers.

After a field visit the final sampling location have been selected. The locations are presented in Table 1

Table 1 Selected locations for passive sampling

SL_ID	River Name	Tentative Strategic Locations	Pollution Sources	Industry	Tannery and Dying factory	Power plant	Household	Fish farms	Agriculture	Fertilizer industry
1	Buriganga	Mirpur Bridge	The widespread waste dumping site of Dhaka City located beside N.R. CNG Filling Station at Savar comprises all kinds' wastes, and chemicals used in agricultural field) as well as other industrial pollutants are major sources.	X					X	
2		Hazaribagh	Tannery and dying factories are the industries from where pollutants come and pollutes the water of Buriganga. But, many of the tannery industries started to shift to Horindhora, Hemayetpur.		X					
3		Chandni Ghat	A channel through Hazaribagh, Hasannagar and Lalbagh area meets with Buriganga at Chandnighat location. Effluents from Hazaribagh industries mix with Buriganga river at this location. Four effluent outlets are found here.	X						
4		Postagola Bridge	Bangladesh-China Friendship Bridge is located in industrial concentrated areas. The major portions of the industries located here are of red categories. A number of effluent outlets for industrial wastage discharge are found at this location.	X						
5		Fatullah	Pollutants from agricultural land, industry, and commercial fish farming like Pangas Farm are major concerns of water pollution at this location.	X				X	X	
6	Shitalakhya	Demra Ghat	Balu river joins with Shitalakhya river at Demra Ghat point. Heavy industrial effluents are discharged at Demra Ghat point. Major industries	X	X					

			are rerolling steel mills, textile, dyeing, plastic and polymers, fiber glass, jute mills and others.							
7		Port Road	A canal from Hajiganj area meets with Shitalakhya carrying industrial pollutants. Many industries are concentrated around this location and these are fibre glass, screen printing, washing plants, pharmaceuticals, knit wears, garments.	**x**						
8		Ghorashal Bridge	The major source of water pollution is Ghorashal Fertilizer Industry at this location. Agricultural pollutants also mix with water here from the surrounding agricultural field.						**x**	**x**
9	Turag	BIWTA Landing Station, Ashulia	Pollution sources are agricultural practice and industrial effluent discharge via different channels.	**x**					**x**	
10	Balu	Ittakhola	Sewerage effluent from Dhaka city through Balu canal and surrounding industrial effluents are responsible for water pollution.	**x**			**x**			

3.3 Deployment of the samplers

Locally made stainless steel racks have been used to deploy the samplers. These are placed in accessible locations. To prevent theft and vandalism, security guards from the local community have been appointed to keep an eye on the samplers.

Figure 6 Installation of passive samplers

The samplers have been deployed for approximately 40 days both during the monsoon as during the dry season. Table 2 and Table 3 show date and time of installation and collection of the samplers. In both season the samplers have been deployed for approximately 40 days. Also, an indication is given of any fouling on the samplers and the colour of the fouling.

Table 2 Installation and collection time of the samplers round 1

1st Round

SL ID	Location	Name of River	Date of Installation	Installation Time	Date of Collection	Collection Time	Algae/nematoda/ Snails	Color
1	Mirpur Bridge	Buriganga	27/02/2020	12:05 PM	08/04/2020	5:30 PM	Few algae	No color
2	Hazaribag	Buriganga	27/02/2020	1:30 PM	08/04/2020	4:15 PM	Few algae	No color
3	Chandni Ghat	Buriganga	27/02/2020	3:20 PM	08/04/2020	3:30 PM	Few algae	No color
4	Postagola Bridge	Buriganga	29/02/2020	9:40 AM	08/04/2020	2:00 PM	Few algae	No color
5	Futtulah	Buriganga	29/02/2020	11:15 AM	08/04/2020	12:50 PM	Few algae	Black
6	Demra Ghat	Shitalakhya	26/02/2020	12:30 PM	08/04/2020	8:30 AM	Few algae	No color
7	Port Road	Shitalakhya	29/02/2020	12:15 PM	08/04/2020	12:05 PM	Few algae	No color
8	Ghorashal Bridge	Shitalakhya	26/02/2020	2:40 PM	08/04/2020	9:45 AM	some algae, namatods and sanails	Brow
9	BIWTA Landing Station, Ashulia	Turag	27/02/2020	10:15 AM	08/04/2020	6:15 PM	Few algae	No color
10	Ittakhola	Balu	26/02/2020	10:40 AM	08/04/2020	7:30 AM	Few algae	No color

During the 2nd round two samplers at the locations have been lost (see Table 3).

Table 3 Installation and collection time of the samplers round 2

2nd Round

SL ID	Location	Name of River	Date of Installation	Installation Time	Date of Collection	Collection Time	Algae/nematoda/Snails	Color
1	Mirpur Bridge	Buriganga	20/09/2020	11:05 AM	29/10/2020	11:30 AM	Moderate Algae, moderate snails, moderate nematoda	
2	Hazaribag	Buriganga	20/09/2020	10:00 AM	29/10/2020	10:15 AM	Few Algae	No color
3	Chandni Ghat	Buriganga	20/09/2020	8:52 AM	29/10/2020	9:20 AM	Few Algae	
4	Postagola Bridge	Buriganga	21/09/2020	9:30 AM	01/11/2020	9:30 AM	Few Algae	
5	Futtulah	Buriganga	21/09/2020	10:15 AM	01/11/2020	Missing		
6	Demra Ghat	Shitalakhya	22/09/2020	10;40 am	31/10/2020	11:15 AM	Few Algae	No color
7	Port Road	Shitalakhya	21/09/2020	12:36 PM	01/11/2020	12:15 AM	Few Algae	
8	Ghorashal Bridge	Shitalakhya	23/09/2020	12:00 PM	31/10/2020	Missing		
9	BIWTA Landing Station, Ashulia	Turag	20/09/2020	12:07 PM	29/10/2020	12:15 PM	Moderate Algae, Few snails	
10	Ittakhola	Balu	22/09/2020	9:30 AM	31/10/2020	10:00 AM	Moderate Alage, Few snails	Brownish

After collecting the samples, they were stored in a freezer at -20 ℃. All samples were analyzed at once after the second sampling round.

4 SAMPLE PROCESSING AND ANALYSIS

4.1 Selection of the laboratory

The chemical analysis of the samples requires advanced equipment (GC-ECD and GC-MS) and qualified staff to measure the contaminants. A visit was made to the laboratories of the DoE and DWASA to check whether the necessary equipment is available. In both laboratories required equipment is not operational and there is insufficient capacity to perform the analyses. The IWM laboratory also does not have the necessary equipment.

It was decided to have the analysis performed by Plasma Plus, part of the IUB. A visit was made to their laboratory, where the equipment and staff present were assessed. The assessment showed that Plasma Plus has the necessary equipment that it is operational and that sufficiently qualified staff is available to perform the analyses.

An agreement has been concluded with Plasma Plus to perform the analysis. In addition, a protocol has been drawn up for sample processing and analysis. Deltares staff provided remote training and guidance for performing the analysis.

Figure 7 Assessment of the Plasma Plus laboratory at the Independent University of Bangladesh

4.2 Selection of contaminants.

The plan was to analyze the samples for a broad spectrum of contaminants including pesticides and pharmaceuticals. Problem is that not all standards needed for the analysis are readily available in Bangladesh and must therefore be imported. This entails high costs. It has therefore been decided to limit the analysis program to Organochlorine Pesticides (OCPs). These are generally pesticides whose use is banned and therefore less used. The list of OCPs analyzed is presented in Table 4.

Table 4 List of OCPs analysed

1	aldrin
2	cis-chlordane
3	trans-chlordane
4	2,4'-DDD
5	4,4'-DDD
6	2,4'-DDE
7	4,4'-DDE
8	2,4'-DDT
9	4,4'- DDT
10	Dieldrin
11	Endosulfan I (alfa)
12	Endosulfan II (beta)
13	Endosulfan sulfate
14	Endrin
15	alfa-HCH
16	beta-HCH
17	gamma-HCH (Lindane)
18	delta-HCH
19	heptachlor
20	heptachlor exo-epoxide (isomer B)
21	hexachlorobenzene
22	hexachloro-1,3-butadiene
23	isodrin
24	pentachlorobenzene

In addition, the samples have also been analyzed for of Polychlorinated biphenyls (PCBs). These substances served as Performance Reference Compounds (PRCs) and are analysed to calculate the concentrations in the water. The sampled volume on the silicone sheet is calculated using the Performance Reference Compounds (PRCs). The PRCs are substances that are added to the Silicone rubbers prior to deployment. After deployment aqueous concentrations of the compounds on the Silicone rubber are back-calculated from concentrations on the silicone rubber, based on the dissipation rates and the physical-chemical properties of the different PRCs using the uptake model for silicone rubbers as described in Booij et al.(1998)1 and Huckins et al.(2002). The PCRs are substances that are not found as pollution in the environment because they are not discharged. This allows them to be used to calculate water concentrations.

Table 5 Polychlorinated biphenyls (PCBs) used as Performance Reference Compounds (PRCs)

1	biphenyl-d10 (PRC)
2	PCB 1 (PRC)
3	PCB-2 (PRC)
4	PCB-3 (PRC)
5	PCB-10 (PRC)
6	PCB-14 (PRC)
7	PCB-30 (PRC)
8	PCB-50 (PRC)
9	PCB-21 (PRC)
10	PCB-104 (PRC)
11	PCB-55 (PRC)
12	PCB-78 (PRC)
13	PCB-145 (PRC)
14	PCB-204 (PRC)

In addition, the samples were analyzed for a number of PCBs that do occur as contaminants in the environment (Table 6).

Table 6 List of PCBs

1	PCB-28
2	PCB-52
3	PCB-101
4	PCB-118
5	PCB-153
6	PCB-138
7	PCB-180

4.3 Sample extraction and analysis

The silicon rubbers have been extracted according to the protocol provided (see 0). The extracts have been analyzed according to the Procedure for the Analysis of Persistent Organic Pollutants in Environmental and Human Matrices as has been prepared for the implementation of the Global Monitoring Plan under the Stockholm Convention (UNEP 2013).

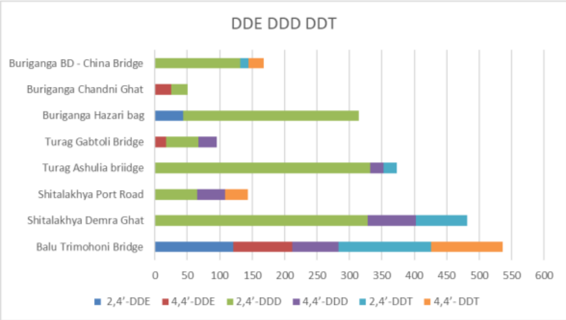
5 RESULTS

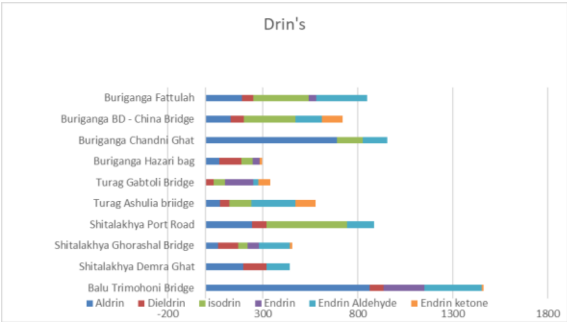
Due to the accuracy of the analysis method, it has not been possible to determine the PRCs levels with sufficient accuracy. The measured amounts were in some cases even higher than the pre-added amounts with which the silicone rubbers were spiked. Therefore, it was not possible to determine the concentrations of the contaminants, because the accuracy of the analysis method was insufficient to determine the level of PCRs with which the passive samplers were spiked. Hence it was only possible to determine the amount adsorbed on the rubber sheets. The amount accumulated depends on the duration of the exposure, the level of contamination and the amount of water that has passed through the samplers. The accumulated amount is standardized on an exposure time of 1 day. It has therefore been calculated how much of a contaminant accumulates on the rubber sheets per day.

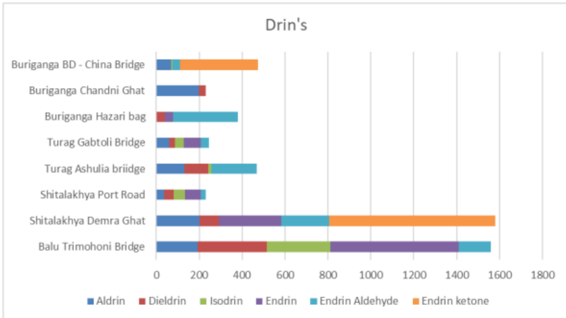
The fact that concentrations cannot be calculated makes it difficult to interpret the results. It is not possible to compare the sampling locations with each other. A comparison between the seasons is also not possible, because both the amount of water that has passed through and the concentrations to which the samplers are exposed can vary.

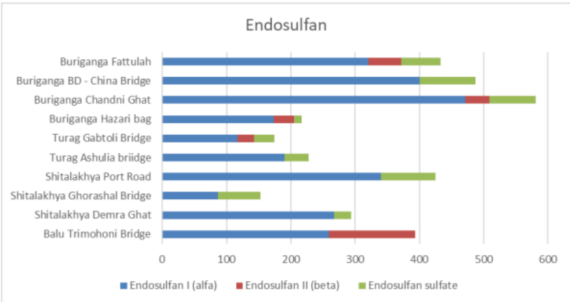
However, the presence of the contaminants can be determined, and the accumulated amounts can be compared with each other. This allows hotspots to be identified and the amounts can be related to potential sources. In addition, the accumulated amount is a measure of the ecological impact.

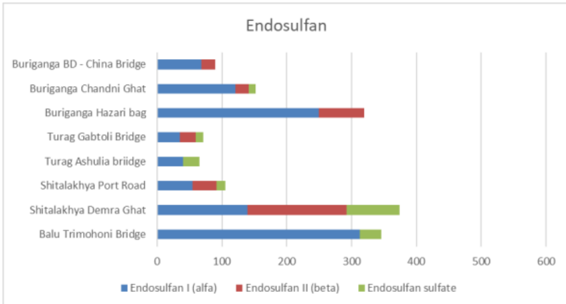
Figure 8 presents the results for the 2 sampling rounds.


DDE DDD DDT
Buriganga BD - China Bridge
Buriganga Chandni Ghat
Buriganga Hazari bag
Turag Gabtoli Bridge
Turag Ashulia briidge
Shitalakhya Port Road
Shitalakhya Demra Ghat
Balu Trimohoni Bridge
0 50 100 150 200 250 300 350 400 450 500 550 600
2,4'-DDE 4,4'-DDE 2,4'-DDD 4,4'-DDD 2,4'-DDT 4,4'-DDT


Drin's
Buriganga Fattulah
Buriganga BD - China Bridge
Buriganga Chandni Ghat
Buriganga Hazari bag
Turag Gabtoli Bridge
Turag Ashulia briidge
Shitalakhya Port Road
Shitalakhya Ghorashal Bridge
Shitalakhya Demra Ghat
Balu Trimohoni Bridge
Aldrin Dieldrin isodrin Endrin Endrin Aldehyde Endrin ketone
-200 300 800 1300 1800


Drin's
Buriganga BD - China Bridge
Buriganga Chandni Ghat
Buriganga Hazari bag
Turag Gabtoli Bridge
Turag Ashulia briidge
Shitalakhya Port Road
Shitalakhya Demra Ghat
Balu Trimohoni Bridge
0 200 400 600 800 1000 1200 1400 1600 1800
Aldrin Dieldrin Isodrin Endrin Endrin Aldehyde Endrin ketone


Endosulfan
Buriganga Fattulah
Buriganga BD - China Bridge
Buriganga Chandni Ghat
Buriganga Hazari bag
Turag Gabtoli Bridge
Turag Ashulia briidge
Shitalakhya Port Road
Shitalakhya Ghorashal Bridge
Shitalakhya Demra Ghat
Balu Trimohoni Bridge
0 100 200 300 400 500 600
Endosulfan I (alfa) Endosulfan II (beta) Endosulfan sulfate


Endosulfan
Buriganga BD - China Bridge
Buriganga Chandni Ghat
Buriganga Hazari bag
Turag Gabtoli Bridge
Turag Ashulia briidge
Shitalakhya Port Road
Shitalakhya Demra Ghat
Balu Trimohoni Bridge
0 100 200 300 400 500 600
Endosulfan I (alfa) Endosulfan II (beta) Endosulfan sulfate

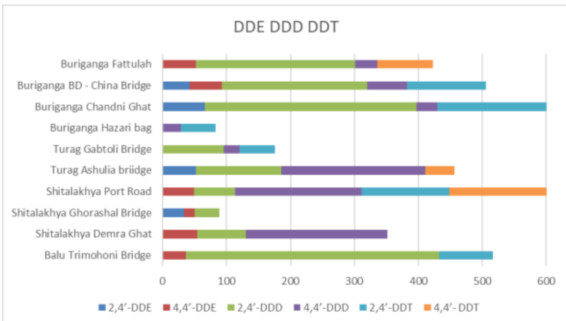

DDE DDD DDT
Buriganga Fattulah
Buriganga BD - China Bridge
Buriganga Chandni Ghat
Buriganga Hazari bag
Turag Gabtoli Bridge
Turag Ashulia briidge
Shitalakhya Port Road
Shitalakhya Ghorashal Bridge
Shitalakhya Demra Ghat
Balu Trimohoni Bridge
0 100 200 300 400 500 600
2,4'-DDE 4,4'-DDE 2,4'-DDD 4,4'-DDD 2,4'-DDT 4,4'-DDT

Figure 8 Accumulated pollutants on the passive sampler silicon sheets in ng/day (left round 1, right round 2)

Table 7 Use sources and impact of pollutants monitored.

Compound	Use	Sources/Impact	Regulation
PCB (Polychlorinated biphenyls)	PCBs products have widely been used as dielectric and coolant fluids in electrical apparatus and in heat transfer fluids.	PCB's are a highly toxic and due to their persistence can be found all over the world. PCBs do not readily break down and therefore	The production has been banned in the United States by the federal law in 1978, and by the Stockholm

Compound	Use	Sources/Impact	Regulation
		may remain for very long periods of time. They accumulate in the food chain and in sediments. At present PCBs can be released to the environment from accidental spills and leaks in transformers, capacitors, or other products containing PCBs. PCBs may be released into the environment by the burning of some wastes in municipal and industrial incinerators and from landfills.	Convention on Persistent Organic Pollutants in 2001
Chlorobenzene			
Pentachlorobenzene	Pentachlorobenzene has been used as a fire retardant as well as an intermediate in the synthesis of, and has occurred as a contaminant in, several chlorinated pesticides and pesticide-related chemicals.	Pentachlorobenzene is a persistent organic pollutant and accumulates in the food chain. It is very toxic to aquatic organisms. The largest current emission source of pentachlorobenzene to the environment occurs through formation in various combustion processes involving solid waste incineration, combustion of coal and combustion of various biomasses.	The product has been banned globally by the Stockholm Convention on Persistent Organic Pollutants in 2009.
Hexachlorobenzene	Hexachlorobenzene was used as a fungicide to protect the seeds of onions and sorghum, wheat, and other grains against fungus. It was also used as a chemical intermediate in	Hexachlorobenzene is very toxic to aquatic life and has long lasting effects to the aquatic environment. It is very persistent. It has a half-life in the soil of between 3 and 6 years.	The trade is regulated by the Rotterdam convention on Prior Informed Consent which entered into force on 24 February 2004. The use and production hexachlorobenzene is severely restricted by the

Compound	Use	Sources/Impact	Regulation
	the manufacture of dyes, synthesis of organic chemicals, rubber and in wood preservation.	Risk of bioaccumulation in an aquatic species is high.	Stockholm convention on persistent organic pollutants, in 2004.
DDE, DDD, DDT	DDT originally has been developed as an insecticide. It has been used in agriculture and to limit the spread of the insect-borne diseases malaria and typhus among civilians and troops. There are indications that is some developing countries and also in Bangladesh it is still used by fishers and dry fish stockers as a preserver (Md Nurul Huda Bhuiyan, 2012).	From 1950 to 1980, DDT was extensively used in agriculture. It is a persistent organic pollutant that is readily adsorbed to soils and sediments, which can act both as sinks and as long-term sources of exposure affecting organisms. Its breakdown products and metabolites, DDE and DDD, are also persistent and have similar chemical and physical properties. DDT and its breakdown products are accumulating in the food web. DDT is toxic to a wide range of living organisms, including marine animals such as crayfish, daphnids, sea shrimp and many species of fish.	The use in agriculture has been banned globally by the Stockholm Convention on Persistent Organic Pollutants since 2004. DDT still has limited use in disease vector control because of its effectiveness in killing mosquitos and thus reducing malarial infections.
Drins	The drins, aldrin, dieldrin, endrin and isodrin have been developed in the 1940s to provide an alternative to DDT. It used to be commonly used as an insecticide in agriculture and to control malaria spreading mosquitos.	Dieldrin it is a very persistent organic pollutant. It tends to biomagnify as it is passed along the food chain. Long-term exposure has proven toxic to a very wide range of animals including humans. It has been linked to health problems such as Parkinson's, breast cancer, and immune, reproductive, and nervous system	It was banned by the Stockholm Convention on Persistent Organic Pollutants.

Compound	Use	Sources/Impact	Regulation
		damage. It is also an endocrine disruptor.	
Endosulfan	Endosulfan has been used in agriculture around the world to control insect pests.	Endosulfan is semi volatile and persistent. It has a relatively high potential to bioaccumulate in fish. It is also toxic to amphibians.	Banned under the Stockholm Convention in since mid-2012
HCH Hexachlorocyclohexane	Lindane (γ-HCH) has been used both as an agricultural insecticide and as a pharmaceutical treatment for lice and scabies. The isomers alpha-HCH and beta-HCH are more toxic than lindane and are by products of lindane production.	Lindane is a persistent organic pollutant: it is relatively long-lived in the environment. It can bioaccumulate in food chains, though it is rapidly eliminated when exposure is discontinued.	In 2009, the production and agricultural use of lindane was banned under the Stockholm Convention on persistent organic pollutants.
Heptachlor	Heptachlor is an organochlorine compound that was used as an insecticide.	Heptachlor is persistent organic pollutant. Heptachlor is lipophilic and poorly soluble in water thus it tends to accumulate in the body fat of humans and animals. Heptachlor epoxide is more likely to be found in the environment than its parent compound. The epoxide also dissolves more easily in water and is more persistent.	The Stockholm treaty of 2001 restricted or banned the use of heptachlor.
Chlordane	Chlordane is an organochlorine compound that was used as a pesticide. In the United States, chlordane was used for termite-treatment of approximately 30 million homes until it was banned	It is resistant to degradation in the environment and in humans/animals and readily accumulates in lipids (fats) of humans and animals. Exposure to the compound has been linked	In 2001 banned by the Stockholm Convention on Persistent Organic Pollutants.

Compound	Use	Sources/Impact	Regulation
	in 1988. Chlordane also has been used in a wide variety of other crops.	to cancers, diabetes, and neurological disorders.	
Methoxychlor	Methoxychlor is used to protect crops, ornamentals, livestock, and pets against fleas, mosquitoes, cockroaches, and other insects. It was intended to be a replacement for DDT.	The compound shows acute toxicity, bioaccumulation, and endocrine disruption activity.	Proposed for a ban under the Stockholm Convention on Persistent Organic Pollutants 2022.

The Government of Bangladesh has adopted measures for preventing the inappropriate use of pesticides and ensure food safety. Already in 1998, registration of more than twenty pesticides, including seven Persistent Organic Pollutants (POPs) pesticides (DDT, endrin, aldrin, dieldrin, chlordane, heptachlor and BHC) and all WHO Class 1a and 1b active ingredients, have been cancelled. In May 2001 Bangladesh has signed the Stockholm Convention on Persistent Organic Pollutants. As a party and signatory nation to the Stockholm Convention, Bangladesh have taken actions on the following activities:

- Generate awareness of the harmful consequences of POPs to reduce their release
- Create legal bindings for their ultimate elimination. No pesticides and insecticides are registered without reviewing the available toxicological and eco-toxicological information of the candidate pesticide.

Despite the policy and regulations, the result of the monitoring shows that several of the OCP are still present in the rivers in and around Dhaka.

6 CAPACITY BUILDING AND DISSEMINATION

During the Dhaka Water Knowledge Days in October 2019 two events took place:

- October 27 – 29 a training was given on the use of passive sampling. The event included classroom training, field training and a visit of the laboratories of IWM, DoE and Plasma Plus. The program of training event is presented in 0. About 10 participants from IWM/CEGIS and Plasma Plus followed the training.
- On October 30 a workshop was held on the Innovative monitoring of organic micro pollutants. A presentation was given on the use of passive sampling and an interactive workshop was held on the needs for routine monitoring of organic micro pollutants and potential use of passive sampling in Bangladesh. The workshop was attended by approximately 30 people, mainly from research institutes, universities and NGOs's.

During the project on the job training was provided to the staff of Plasma Plus Laboratory. Due to Covid19 the training was online. Several online sessions have been held to discuss the preparation and analysis of the samples and the interpretation of the results.

During the Delta Knowledge Days in September 2022 the results of the project have been presented during the parallel session on Clean and safe water on September 17. Approximately 50 participants joined the session (including representatives of DoE, DWASA and the private sector).

Several attempts have been made to involve the DOE's laboratory in the project. The DoE staff has been invited to the training courses and workshop in October 2019. An attempt has also been made to organize separate workshops with DOE staff. However, due to administrative procedures between the ERD, the MoEFF&CC and the DOE, it has not been possible to fully involve the DOE as a key knowledge customer in the project. This despite the fact that individual employees showed a genuine interest in the project. This is also apparent from the fact that during the final presentation 3 delegates from the DOE took note of the results and actively participated in the discussion.

7 IMPLEMENTATION OF ROUTINE MONITORING

This project shows that the problems with the contamination of organic micro-pollutants in the rivers in and around Dhaka are serious. In this project we limited ourselves to the analysis of OCP and PCBs. Other project-based research also shows that there are problems with other hazardous substances. In 2019, for example, a broad screening was performed for emerging compounds in the Meghna (Deltares, 2018). Using passive sampling, samples were examined for 340 substances at a number of locations in the Meghna, near Bishnondi. In total, a total of 87 substances were found, including PCBs, PAHs, OCP, other pesticides and pharmaceuticals. Chowdhury et al., 2012 found Organophosphorus and carbamate pesticide residues in surface water in the Savar and Dhamrai Upazilas. A study by Anwar Hossain et al. (2018) showed occurrence and ecological risk of pharmaceuticals in river surface water of Bangladesh.

All these pollutants have an impact on both the ecosystem and the public health. To develop strategies for pollution control and plan future investments in wastewater and drinking water treatment technology regular monitoring programs for these types of pollutants are required. This requires a laboratory that is specialized in performing such analyses. Not just on a project basis but on a routine basis. Implementation of routine monitoring of emerging pollutants requires ownership by of a responsible authority. DoE, being responsible for water quality monitoring is the most appropriate authority to carry out such a monitoring program.

Implementation requires:

Trained staff for:

- Sampling
- Performing the analyses
- Interpreting and reporting the results.

A laboratory that is able to do the analysis on a routine base, should be equipped with GC-ECD, GC-MS and having sufficient equipment and chemicals for sample preparation and analysis. In particular high-quality standard should be available to allow for the determination of a broad spectrum of emerging pollutants. Hence significant investments in facilities, equipment and supplies as well as human resources are required, requiring a significant period of catalytic support from development partners, to upgrade the capacity of the DoE, and make it operational. This effort, however, needs to be accompanied by improving the legislative framework and providing sufficient public funding to maintain operational surveillance and monitoring activities.

As an alternative, the analysis can be performed by commercial laboratories. As has also been done in this project. Sampling and analysis of 10 sites in the rivers around Dhaka cost approximately US$20,000 per year, sampling twice a year. However, upscaling to nationwide monitoring required a multiple of that. At the moment this also requires training and upgrading of these commercial laboratories. These labs require significant investments in equipment and consumables to perform these analysis on a routine basis. This requires long-term contracts with the government to make this possible.

The question is therefore whether this should be left to the market or whether it is a public task. The advantage of the latter model is that there is a better guarantee of continuity and that the knowledge for the interpretation, processing and reporting of the results is also available with the responsible authorities.

The operational cost will be highly dependent on the number of samples processed. The investment required will depend of the available laboratory infrastructure. A more detailed investment plan has to be made. This is not in the scope of this project.

7.1 Regulatory aspects of the use of Passive Sampling

As noted in chapter 2, an important advantage of using passive samplers is that the results are averaged over time. This means that fewer samples need to be taken to get a representative picture of the contaminations. This leads to considerable cost savings.

However, the use of passive samplers is not universally accepted as a formal method. In many national and international regulations, the sampling protocols are based on grab sampling. For example, the official instructions for monitoring under the European Water Framework Directive are based on grab samples. The sampling protocols under the Stockholm Convention for POPs also do not allow the use of passive sampling. Nevertheless, passive sampling is increasingly being used in many countries and there is much discussion about including its use in sampling protocols.

8 CONCLUSION AND RECOMMENDATIONS

In Bangladesh there is no routine monitoring of emerging compounds such as pesticides, pharmaceuticals, steroids, endocrine disruptors, hormones, industrial additives and chemicals. This project and other project-based research show that there are severe problems with pollution of these type of compounds. In order to develop policies for pollution control, it is necessary to have insight into the nature and extent of the problems.

In this project we investigated to what extent the use of passive sampling can be used to implement routine monitoring of emerging compound in Bangladesh.

During the project we encountered two limitations, as a result of which the goal of the project was not achieved completely. One is the availability of high-quality standards required for the analyses. As a result, a broad screening of emerging compounds was not possible, and we had to limit ourselves to OCPs. In addition, the equipment present was not sensitive enough to measure the PCBs used as PRCs with sufficient accuracy. As a result, it was not possible to determine the concentrations of the measured substances. However, the amounts of adsorbed material have been determined. This provides insight into the occurrence of the contaminants and their potential ecological impact.

The analysis can be performed by a commercial laboratory, but also by a public authority. In view of the tasks of the DoE, it is obvious that the DoE will undertake the implementation of such a monitoring programme. This requires investments in both staff and equipment. For implementation, a legal framework must be established, and sufficient public funds must be made available for the execution of the monitoring program. Intensive training and guidance over a longer period by a development partner can be helpful in this regard.

Although the use of passive samplers is cost effective, it should be noted that sampling protocols in regulations are based on grab sampling. However, in many countries the use of passive samplers is increasing and there is discussion about including their use in sampling protocols.

9 REFERENCES

Chemicals Branch United Nations Environment Programme (UNEP) Division of Technology, Industry and Economics Geneva November 2013, Procedure for the Analysis of Persistent Organic Pollutants in Environmental and Human Matrices to Implement the Global Monitoring Plan under the Stockholm Convention Protocol 2: Protocol for the Analysis of Polychlorinated Biphenyls (PCB) and Organochlorine Pesticides (OCP) in Human Milk, Air and Human Serum

Chowdhury A.Z., M.N. Islam, M. Moniruzzaman, S.H. Gan, M.K. Alam, Organochlorine insecticide residues are found in surface, irrigated water samples from several districts in Bangladesh, Bull. Environ. Contam. Toxicol. (2013),10.1007/s00128-012-0897-z

M.A.Z. Chowdhury, S. Banik, B. Uddin, M. Moniruzzaman, N. Karim, S.H. Gan, Organophosphorus and carbamate pesticide residues detected in water samples collected from paddy and vegetable fields of the Savar and Dhamrai Upazilas in Bangladesh, Int. J. Environ. Res. Public Health., 9 (2012), pp. 3318-3329, 10.3390/ijerph9093318

Deltares, Monitoring of hazardous pollutants in the Meghna river, Bangladesh, TA-8803 BAN: Strengthening Monitoring and Enforcement in the Meghna River for Dhaka's Sustainable Water Supply, Asian Development Bank, 2018

Anwar Hossain, Shihori Nakamichi, Md. Habibullah-Al-Mamun, Keiichiro Tani, Shigeki Masunaga, Hiroyuki Matsuda. Occurrence and ecological risk of pharmaceuticals in river surface water of Bangladesh, Environmental Research, Volume 165, August 2018, Pages 258-266

Booij, K., Sleiderink, H.M., Smedes, F., 1998. Calibrating the uptake kinetics of semipermeable membrane devices using exposure standards. Environmental Toxicology and Chemistry, vol. 17, pp 1236-1245.

Huckins, J., Petty, J, Lebo, J., Almeida, F., Booij, K., Alvarez, D., Cranor, W., Clark, R., Mogensen, B., 2002. Development of the Permeability/Performance Reference Compound Approach for In Situ Calibration of Semipermeable Membrane Devices. Environmental Science & Technology, vol 36, pp 85- 91

Annex A Protocol for extraction silicone rubber passive samplers.

materials:

- hexane (J.T.Baker, ULTRA-grade)
- acetonitrile (J.T.Baker, LCMS-grade)
- methnol (ULTRA-grade)
- diethylether (J.T.Baker, ULTRA-grade)
- Sodium sulphate (Merck, proanalyse)
- florisil (Sigma-Aldrich)

reagentia :

- florisil: Florisil is dehydrated by heating during 16 hours in an oven at 150 °C followed by cooling down in a desiccator. Store erlenmeyer with stopper

Sodium sulphate: Na_2SO_4 is dehydrated by heating in at 250 °C for 16 hours followed by cooling down in a desiccator. Store erlenmeyer with stopper

Sampler preparation:

- Clean and dry the six silicone rubber sheets that form on sampler samplers in such a way that all the water and algae or other organics material are removed from the sampler as much as possible.
- Weigh the six silicone sheets and record the total weight (one sampler exists of a couple of sheets, mainly six)
- Fold the six silicone sheets in harmonica form and put them by using a long pair of tweezers into 300 ml Erlenmeyer
- Add to the silicone sheets the following internal standards (IS):

1. If possible internal standard 13C-PCB
2. Internal standard normally used for the GC-ECD analysis of the organic compounds (13 C labelled or deuterated)

- Add a standard (SA) to a blank sampler containing the compounds that also will be analysed on the samplers that were deployed.

Sampler extraction:

- Extract the sheets for 2 days on a rotation shaker with 75 ml acetonitrile (110 rpm).
- Transfer the acetonitrile after two days into a round bottom flask.

- Add again 75 ml acetonitrile to the sheets and extract another 2 days. Combine the both dialysis extracts.
- Concentrate the combined extract by rotavapor evaporation at 45 °C and 450 mbar to 1-2 ml.
- Split the extract in to equal portions by weight.
- Store one of the two acetonitrile extracts in a freezer at -18°C (these extracts might be used for probable future analysis on LC-compounds
-

Preparing extracts in hexane for GC-analysis:

- Use the other half of the extract.
- Add 100 ml hexane to 1 ml ACN-extract (so if the extract has only a volume of 0,5 ml, then add 50 ml)
- Shake well
- Concentrate to 1 a 2 ml by rotavapor evaporation at 45 °C and 195 mbar
- If a water droplet is visible add a little bit of the dehydrated sodium sulphate.
- Transfer the extract to a point tube
- Rinse the sodium sulphate (if used) three times
- Concentrate the hexane to approx 100-200 ul.
- Transfer to a crimp cap or screw cap to store the extract in,
- rinse the point tube, transfer to the storage vial and fill up to finally an extract of exactly 1 ml
- store the vial in a freezer at -18°C until further analysis

3. Quality control:

Control 1: Use for every series at least 1 reference silicone rubber sampler to determine the original amount of PRCs.

Control 2: Treat for every series also a blank solvent

Annex B Program: Training on the use of passive sampling

JPC Water Quality, Part of WP3, Pillar 1: Urban Water Quality Management for Dhaka City

When: Sunday 27th and Monday 28th (and optional Tuesday 29th) of October

Where: Lakeshore Hotel, Gulshan, Dhaka,

Room: Akota

Sunday 27th of October: Class room training

9.00: Welcome

9.30-10.00: Joining the opening of the Dhaka Water Knowledge Days by the ambassador of the Netherlands

10.15-11.30: Introduction on Passive sampling with some examples of use (I)

11.30-12.00: Tea break

12.00-13.30: Extraction and data-analysis + Uptake principles of silicone rubber samplers

13:30-14:30: Lunch

15:00-16.00: Practice data handling silicone rubber samplers

16.00-16.45: Short break

16.45-17.00: Uptake principles of Speedisk sampler and practice data handling

Monday 28th of October: Field training

9.00h: Gather at the front door of the Lakeshore hotel

9.30h: Leave for the field trip to visit two locations for demonstration of the deployment of the passive samplers

On the way there will be lunch. We expect to be back at the location at 17.00h

Tuesday 29th of October: Visit of laboratories

This day is optional to the persons who are not connected to one of the visiting laboratories. Others will join this visit to show the laboratories and discuss the possibilities for the extraction and analysis of the passive samplers in the future monitoring project.

For the people who will not join, they can visit the Dhaka Water Knowledge Days.

Wednesday 30th of October:

10.00-11.30: Joining the workshop on the Dhaka Knowledge Days: Innovative monitoring of organic micro – pollutants (Room: Ikenana 1)