The Fate of Chromium in Wastewater Treatment and Reuse, and the associated occupation health risks in Kanpur, India

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Abstract

The present study explored the fate of chromium in wastewater treatment and reuse and the associated occupational health risks in Kanpur, India. The case study area, Kanpur, is the biggest city in the state of Uttar Pradesh, and it is known for its leather industry. There are two sewage treatment plants (STPs) and one common effluent treatment plant (CETP) in Jajmau, a leather industrial area. The 130 MLD Jajmau STP, initially designed for domestic wastewater treatment, is known to receive illegal tannery discharges rich in chromium (Cr), a carcinogenic heavy metal when present in its hexavalent form [Cr(VI)]. The CETP was constructed to manage both domestic and tannery wastewater. According to previous studies, both plants are poorly operated and exceed the parameters of water quality standards. Moreover, the treated effluent from these facilities is combined and reused for irrigation across 2,500 hectares of farmlands in Kanpur's peri-urban regions, driven by India's water scarcity and the necessity of efficient recycling of treated wastewater.

The study adopted a mass balance approach to track chromium concentrations throughout the 130 MLD Jajmau STP treatment process. It also assessed the occupational health risks of chromium exposure for STP workers and farmers who utilize STP-derived products. Additionally, the study explored how adopting the novel technologies piloted under the Pavitra Ganga project might alter these occupational health risks. Data collection involved a mixed-methods approach, combining qualitative and quantitative data from key informant interviews, structured observations, and chromium analyses. The health risk assessment employed a semi-quantitative approach in line with WHO's wastewater safety plan.

High levels of total chromium in the influent support the hypothesis of illegal tannery discharges. Surprisingly, hexavalent chromium levels, considered more hazardous, remain below 100μg/L, indicating low carcinogenic risks for workers and farmers. Despite significant reductions during treatment, the STP effluent fails to meet permissible total chromium limits for irrigation. Notably, total chromium accumulates in primary sludge, posing environmental and health concerns. Recirculation of activated sludge also impacted chromium accumulation. Health risk assessments reveal occupational and irrigation-related health risks associated with high chromium levels in STP and CETP effluents. Implementing novel technologies could reduce effluent chromium levels, but sludge-related risks for workers remain. Swapping technologies may not substantially reduce farmers' exposure risks, as the primary chromium source is the CETP effluent.

Keywords: *wastewater treatment, chromium, health risks assessment, Kanpur, wastewater safety plant, wastewater reuse*

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Chapter 1. Introduction

This chapter present the background of the study and the research problem. It also states the research questions and objectives of this study.

Background

Water demand is increasing due to human needs regarding municipal water supply, industrial and agricultural activities. From these, agriculture is the most significant global water user. It has been estimated that 44% of global freshwater withdrawals are consumed by agriculture irrigation (38%), municipal water consumption (3%) and industrial water consumption (3%). The remaining 56% of freshwater is a waste product from each water use sector (UN 2017).

In recent years, drivers like population growth, food security, water stress, depletion of groundwater sources and pollution of water bodies have encouraged the use of treated wastewater as a water source. This has led to the development of novel wastewater treatment technologies to produce treated wastewater that can be used for agricultural irrigation or industrial reuse (Drechsel et al. 2010). In parallel, the increase in sludge production from municipal wastewater and conventional treatment and the limited space to dispose of it have opened up the possibility of recycling essential nutrients and producing biosolids, defined as the sludge that has overcome different types of treatment and can be helpful for fertilizer or soil amendment (U.S. EPA 1994). However, industrial wastewater treatment remains a bottleneck for reclaimed water due to its high toxicity and concentration of pollutants (Rao et al. 2012).

India's leather industry is a commercial activity rooted in ancient tanning traditions. There are about 3,000 tanneries across the country, most located along the Ganga River (Dwivedi et al. 2018). Kanpur, located in Uttar Pradesh, has a cluster of more than 400 tanneries at Jajmau that discharge up to 26 MLD of wastewater (Bassi et al. 2019). The many chemicals used during tanning, including dyes, ammonium salts, acids, and heavy metals, represent a source of pollution for land and water bodies and a hazard for local communities (Chaudhary et al. 2017). Chromium is generally used in the tanning process as basic chromium (III) sulphate, and it is a metal of interest due to its toxicity and carcinogenic effects when present as hexavalent chromium Cr (VI) (Chaudhary et al. 2017). Indian standards set a concentration of 2.0 mg/L for total chromium (Cr) and 0.1 mg/L for hexavalent chromium Cr (VI) in inland surface water (MoEFCC 1986).

Kanpur City has four wastewater treatment plants, three of them situated in Jajmau: two sewage treatment plants (STPs) and one common effluent treatment plant (CETP) (Bassi et al. 2019). The CETP treats domestic water and industrial wastewater from the tanneries (JNNURM 2006). The 130 MLD Jajmau STP is supposed to treat only domestic wastewater, but it also receives illegal discharges from tanneries, which has affected its treatment capacity (JNNURM 2006). At the same time, the treated effluent of the STP and the CETP is mixed and used for irrigation in peri-urban areas of Kanpur through a concrete irrigation channel that supplies around 2,500 ha of farmlands (Bassi et al. 2019; Breitenmoser et al. 2022).

Under the Pavitra Ganga project, an EU-India initiative to address wastewater treatment and develop opportunities for water reuse and resource recovery, it has been installed an innovation site in the STP Jajmau I to assess the efficiency of different technologies in wastewater treatment and heavy metals removal such as AndicosTM, constructed wetland plus, self-forming dynamic membrane bioreactor and structured adsorbent(Pavitra Ganga 2020).

Research problem

Between the water demand and the water supply for Kanpur, there is a deficit of 376 million cubic meters (MCM) (Bassi et al. 2019). The total wastewater generation of the Kanpur Metropolitan Area (KMA) is around 767 million litres per day (MLD) (Bassi et al. 2019). Currently, the treated wastewater is conveyed to a concrete irrigation channel for peri-urban reuse in farms (Breitenmoser et al. 2022). The wastewater in the channels is a mix of STP and CETP effluents, with poor water quality and exceeding the parameters for irrigation (Breitenmoser et al. 2022). .Babalola et al. (2023) explored faecal hazards associated with the water reuse scheme in the 130 MLD Jajmau STP. *E. coli* was detected in the effluent above the discharge standards and the guidelines for reuse concentrations, and a semi-quantitative risk assessment was conducted using the sanitation safety plan (SSP) approach for the STP workers and farmers when implementing a novel technology. The novel technology increased the number of health risks but decreased the severity. Regarding the use of wastewater by farmers, the number and severity of risks decrease due to the improvement in effluent quality with the novel technology (Babalola, 2022).

Considering that it is known that tanneries are illegally discharging into sewers and high chromium wastewater is arriving at the 130 MLD Jajmau STP, there is still a gap regarding the studies assessing chemical exposure to wastewater reuse and the initial concentrations and the transformations of total chromium and its carcinogenic speciation Cr(VI) during the treatment process. In addition, there is a lack of information about the fate of sludge after the treatment process and about the effectiveness of the pilot technologies being trialled in chromium removal.

Research justification

The study aims to determine the levels of chromium (Total Cr and Cr(VI)) arriving at the 130 MLD Jajmau STP and assess the impact of the pilot technologies on removing this heavy metal. This is relevant due to the high number of tanneries around Kanpur that discharge heavy metals, organic pollutants and solvents that are discharging into the Jajmau STP. Chromium is a metal of interest due to its toxicity and relation to mutagenic and carcinogenic diseases, specifically hexavalent chromium species. Hence, high chromium concentration in wastewater and sludge represents a potential occupational health risk for STP workers and farmers reusing the mixed effluent. It also aims to assess the occupational health risks for STP workers and farmers regarding exposure to chromium the wastewater and effluent.

Aims

To explore the impact of a novel technology on the removal of chromium and associated occupational health risks in Kanpur, India.

Research objectives and research questions

The specific objectives of this research are:

1. To determine the concentrations of total Cr and Cr (VI) in the influent, effluent and sludge from the different processes of the wastewater treatment plant and the novel technology.
2. To determine the fate of chromium (total Cr and Cr (VI)) in the wastewater treatment plant and the novel technology using a mass balance approach.
3. To evaluate the occupational health risks related chromium for the STP workers and farmers reusing the products from the STP.

4. To explore how occupational health risks related to chromium would change if the piloted technology was implemented.

Research questions

1. What are the concentrations of total Cr and Cr (VI) in the water stream and sludge across the treatment train of the STP and in the novel technologies?
2. How does the fate of chromium (total Cr and Cr (VI)) vary in the wastewater treatment plant and the novel technology, as determined by a mass balance approach?
3. What are the occupational health risks associated with chromium exposure for STP workers and farmers reusing products from the STP?
4. What would be the impact on occupational health risks related to chromium if the piloted technology for wastewater treatment was implemented?

Chapter 2. Literature review

This chapter present an overview of the state of the art of the science for the study. It begins with an overview of wastewater treatment, then wastewater treatment products reuse, occupational health risk considerations on wastewater reuse and finally wastewater reuse in India.

2.1 Wastewater treatment

Despite being a common statement, water is an essential resource for life. Only referring to humans, people need water for as basic day-to-day activities like drinking, cooking, cleaning, hygiene and food production (Gleick 2003). Furthermore, water is necessary for biota and animals to maintain a balance in natural ecosystems. In contemporary societies, it is also required for commercial, institutional and industrial activities (Gleick 2003). It is considered to be wastewater after being used for all kinds of human activities because it contains wastes from households, industries, institutions and commercial businesses.

Wastewater constituents are biodegradable organic carbonaceous materials, microorganisms, nutrients, sulphur components, metals, cellulose, micropollutants and other organic and inorganic materials (Henze et al. 2002)—all of these present different hazards to humans, fauna and flora and the environment.

For that reason, wastewater must be treated with the objectives of removing the biodegradable organic matter and nutrients to avoid oxygen depletion and eutrophication in water streams; inactivating the pathogenic microorganisms to ensure public health; and removing metals, organic and inorganic materials to avoid bioaccumulation in the food chain or toxic effects (Henze et al. 2008). Wastewater treatment involves a series of unit operations and processes to change wastewater’s physical, chemical and biological parameters to make it suitable for disposal or reuse and to prevent human exposure to excreta-related pathogens in excreta and wastewater (Strande et al. 2014).

However, the origin of wastewater can significantly affect the constituents and the treatment needed. Qasim (2017)defines municipal wastewater as liquid waste collected from residential, commercial and industrial areas and transported by a sewerage system to a treatment location. On the other hand, industrial wastewater comprises wastewater generated by companies such as petrochemicals, coal chemicals, food processing, mining, petroleum refining, pharmaceuticals, papermaking, and dying (Henze et al. 2008). It has been reported that industrial wastewater's chemical and biological characteristics are different, such as high toxicity, poor biodegradability, high salinity, oil content, and grease content, so the treatment is generally prolonged and involves additional pre-treatment steps (Henze et al. 2008).

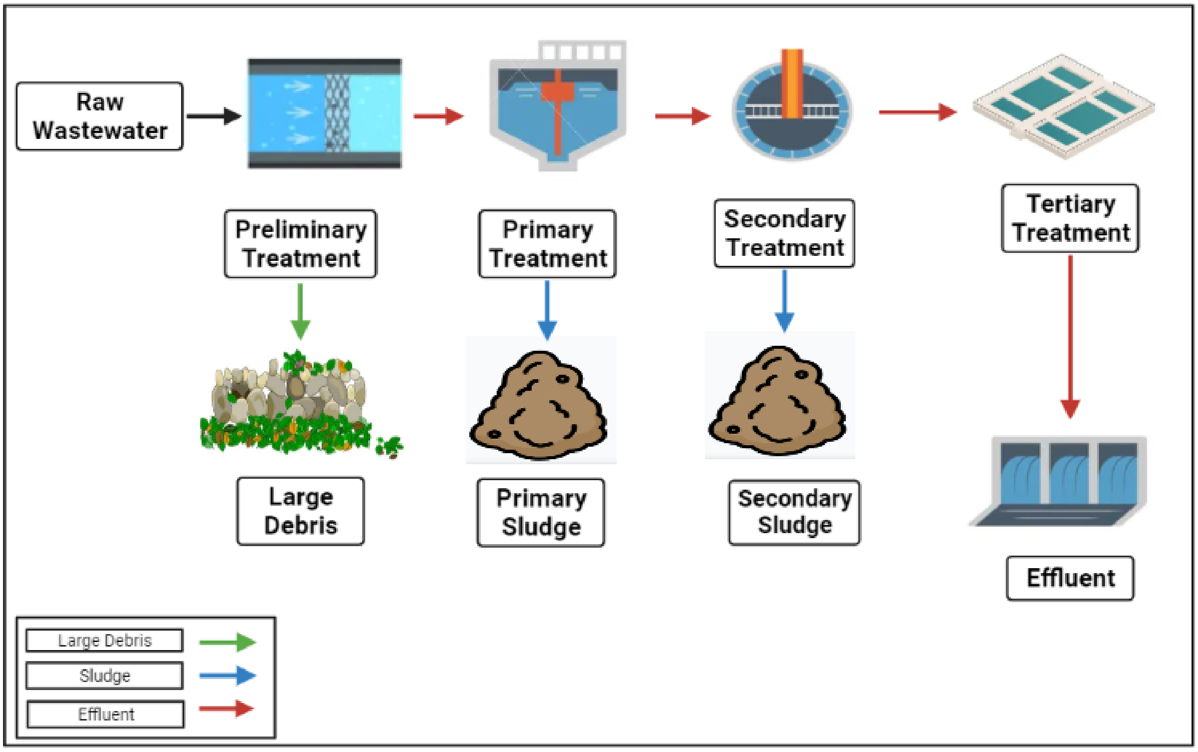
For this reason, it can be challenging to ensure wastewater treatment effectiveness for cities with many industries or industrial waste discharged in a municipal or sewage treatment plant (STP). For instance, Metcalf & Eddy Inc. (2003)points out that some compounds found in industrial wastewater are toxic to microorganisms used in conventional secondary treatment (Section 2.2). Furthermore, considering the expanding pollution potential caused by industrialisation, industrial effluents must be treated before discharging into municipal sewers and water bodies (Rao et al. 2012).

Rao et al. (2012) state that while big industries have effluent treatment plants, this might not be an option for small and medium industries due to the cost. To address this issue, countries like India have established common effluent treatment plants (CETPs) in industrial areas, where industrial effluents are treated in small-scale systems to meet the safe discharge limits (Rao et al. 2012).

2.2 Treatment technologies

Wastewater treatment usually involves the application of physical forces, chemical and biological activity to remove the hazardous constituents of the wastewater so they comply with environmental reuse/disposal standards (Metcalf & Eddy Inc. 2003). The typical treatment train includes preliminary treatment, primary treatment, and secondary treatment, but there is an interest in including tertiary or advanced treatment (Rao et al. 2012). Figure 1 presents an overview of a standard treatment train with inputs and outputs of each step, noting that regarding the water line, the effluent of a step is the input of the following treatment step.

Figure 1. General overview of a standard treatment train



The first step is called preliminary treatment, and its objective is to remove wastewater and sludge constituents such as coarse large or floating materials, debris, oil, and grease (Henze et al. 2008). As a pre-treatment step, this prevents blockages and protects downstream equipment. Tilley et al. (2014) mention that the standard technologies for this step are grease traps, screens and grit chambers.

The primary treatment aims to remove organic and inorganic suspended solids, generally through physical processes for solid-liquid separation (Metcalf & Eddy Inc. 2003). For this purpose, the primary clarifier allows the heavier particles to settle down due to gravity while the lighter particles, debris and oils float on the surface. The design of a clarifier depends on several factors, such as wastewater characteristics, treatment train configuration and operating conditions (Veenstra 1999). However, they typically remove 50-60% of the total suspended solids (TSS) and have a biological oxygen demand (BOD) removal efficiency of 25% - 50% (Metcalf & Eddy Inc. 2003). The most common processes that sludge undergo are dewatering and stabilization to reduce odour, volatile solids content and pathogen levels (Veenstra 1999).

Secondary treatment is necessary to degrade and remove soluble and biodegradable solids through biological treatment (Qasim 2017). The most used technologies nowadays are activated-sludge processes and anaerobic digestion (Metcalf & Eddy Inc. 2003). This step oxidizes the dissolved and particulate biodegradable components. It captures suspended solids into a biological floc and transforms or removes essential nutrients such as nitrogen and phosphorus.

The tertiary or advanced treatment removes residual constituents in wastewater, such as microorganisms, nutrients such as nitrogen and phosphorus and the remaining suspended matter. It is commonly done through chemical processes like disinfection, radiation, chemical oxidation and membrane filtration (Tilley et al. 2014).

2.3 Wastewater products reuse

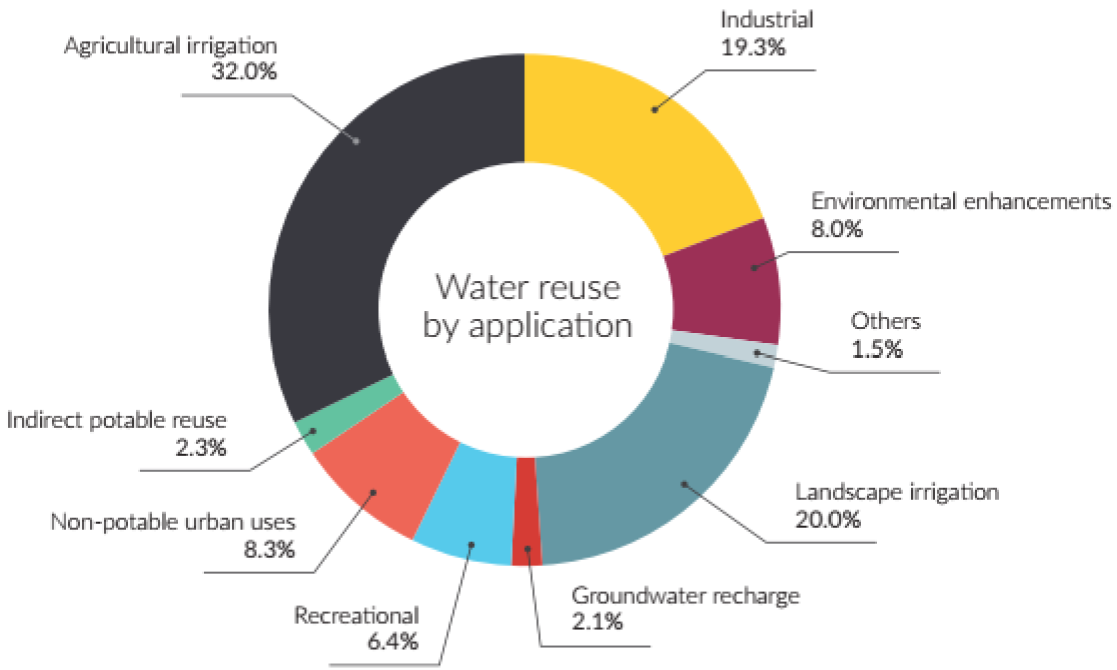
Wastewater and sludge land application were traditional practices in many civilisations due to the known value of excreta as fertiliser (Henze et al. 2008). There is evidence of the use of wastewater for agricultural irrigation up to 5,000 years ago, from China to the civilisation of the Indus Valley as well as Greece and the Euphrates region (Asano and Levine 1996; Henze et al. 2008).

During the first stages of urban sanitation in the 20th century, sewage continued to be spread on the land as fertiliser without proper treatment, and it is still used as a common practice in some countries (WHO 2006). This represents a high risk of exposure to viruses, bacteria, helminths and parasitic protozoa for farmers, consumers and nearby communities (WHO 2006). In contrast, wastewater was also discharged to water bodies that were the source of water supply. To overcome this issue, effluent characteristics standards, water quality objectives, and wastewater management regulations have increased. U.S. regulations include the Clean Water Act (CWA) 1972, the Water Quality Act of 1987 (WQA), the 40 CFR Part 503 (1993), the Total Maximum Daily Load (TDML) (2000) (Metcalf & Eddy Inc., 2003), principally driven by environmental and health concerns.

Parallelly, social and anthropogenic factors such as population growth, the depletion of groundwater sources, the pollution of water bodies and the consequences of climate change on the hydrological water patterns of droughts and floods are some of the drivers for reclaimed water (Metcalf & Eddy Inc. 2003). Drechsel et al. (2010) defined reclaimed water as treated wastewater that can be used for agricultural irrigation or industrial reuse.

Figure 2 displays the sectors that reuse wastewater, noting that only a tiny fraction of the total wastewater generated undergoes tertiary treatment (UN 2017). It is important to note that the sectors that globally demand freshwater such as agriculture and industry, are also the users of reclaimed water. In other words, agriculture is the primary user of freshwater as it is of reclaimed wastewater. For example, the UN (2017) proposes that globally there is potential to irrigate 15% of the lands worldwide with the wastewater discharge by the municipalities.

Figure 2. Global water reuse after tertiary treatment. Source: (UN 2017)



When reclaimed water is used for agricultural purposes, it is important to differentiate between planned and unplanned water reuse, because each of them has its own characteristics (Table 1) and require different risk management approaches (Drechsel et al. 2022) .

Table 1. Characteristics of two principal wastewater irrigation types. Source: (Drechsel et al. 2022)

	Unplanned Use	**Planned Use**
Management status	Unplanned, usually informal farming activities along streams in and downstream urban areas	Planned (formal) water reuse at a particular downstream location of a treatment plant
Reuse guideline availability	Low, need guidance from WHO	High, usually own national guidelines available
Direct versus indirect use	Mostly indirect use of diluted wastewater, in part direct use	Mostly direct use (treated, raw) wastewater, sometimes mixed wastewater and freshwater
Estimated global scale	About 29.3 million hectares	0.7–1.35 million hectares
Climates	All climates, mostly driven by poor sanitation	Mostly arid, but also driven by economic water scarcity
Physical locations	Any open plot near a water body	Near treatment plants to allow wastewater to be channelled to agriculture sites
Official recognition	Low, usually informal sector	High, usually formal sector
Water quality	Varies largely from untreated to (partially) treated to seasonally or generally diluted wastewater with spatial and temporal variations	Relatively smaller variation in treated wastewater quality
Health risk mitigation focus	A combination of risk barriers between farm and fork depending on risk awareness and institutional support	Compliance with Sanitation Safety Plans, incl. water quality monitoring and crop restrictions as additional risk barriers
Existing institutional capacity	Low to moderate; laboratory testing uncommon, except for occasional screening	Moderate to high; laboratory testing of water quality part of a monitoring plan
Risk mitigation challenge	To identify incentives to support adoption of low-cost risk mitigation measures, and related compliance monitoring	To maintain institutional capacities for plant maintenance and effluent monitoring
Main policy challenge	To balance farmer livelihoods and community benefits against risks; to enforce source pollution control	To build wastewater governance for safe and productive reuse; ensuring fit-for-purpose use
Expectations from a Water Reuse Guideline	Risk assessment and mitigation measures which do not require special capacities or data	Water quality thresholds to monitor treatment performance

On the other hand, sludge is disposed of in landfills or incinerated, depending on the country's regulations (U.S. EPA 1994). In recent years, the paradigm has shifted to the reuse of biosolids, defined as the sludge that has overcome different types of treatment and can be helpful for fertiliser, soil amendment for landscaping, or converted into energy and fuel through thermal processes as mentioned above (U.S. EPA 1994; Syed-Hassan et al. 2017).

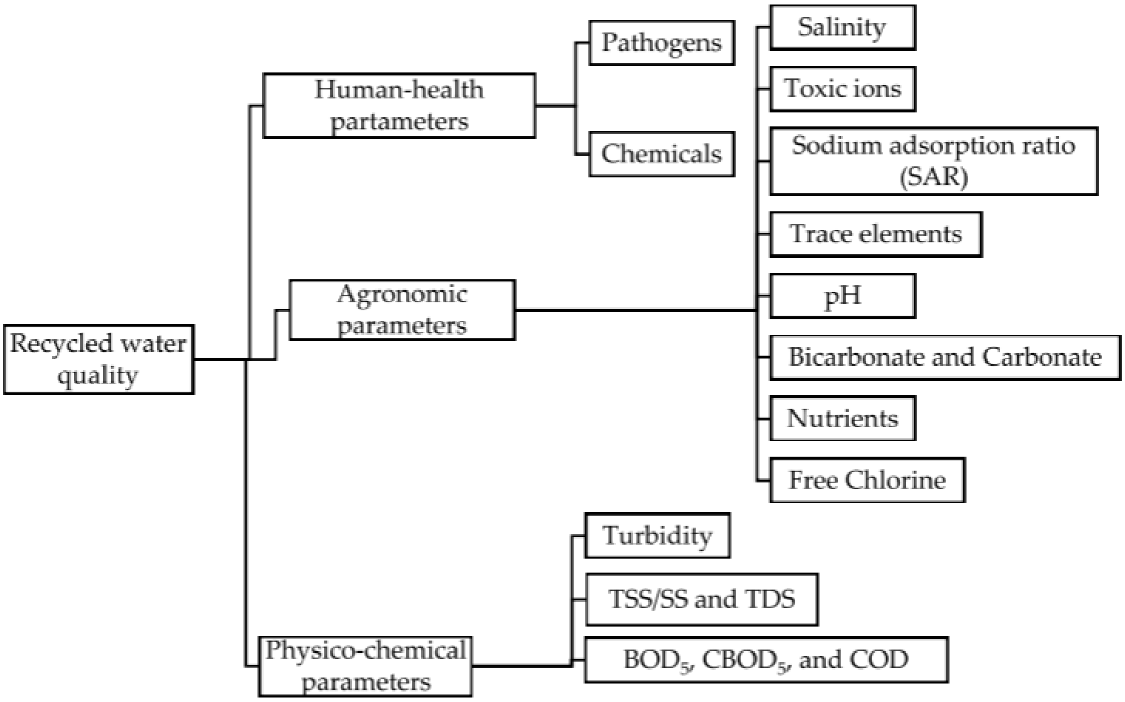
2.3.1. International standards for effluent and sludge.

Considering that agriculture is the main user of water reclamation, different governmental agencies have created regulations for the use of reclaimed water (EPA 2012). The first countries to develop regulations regarding water reclamation were the USA, Mexico, and Italy during the 1970s. However, other international organizations, including WHO, FAO, EPA, ISO standards, and the European Commission, have also issued guidelines on the topic and encouraged countries to do the same (Shoushtarian and Negahban-Azar 2020). The main difference between standards and guidelines is that standards are rules established by authorities; in contrast, guidelines are non-enforceable and describe best practices(Asano et al. 2007).

FAO guidelines classify the application of reclaimed water based on the type of crops and potential exposure of workers and consumers(FAO 1992). It also provides requirements for reused water quality for irrigation according to parameters such as electric conductivity (EC), total dissolved solids (TDS), sodium adsorption ratio (SAR), chloride, nitrogen and bicarbonate (FAO 1992). EPA's guideline specifies requirements and recommendations for different types of reclaimed water regarding required treatment, water quality, limits on chemical constituents, and setback distances for application and monitoring (EPA 2012; Shoushtarian and Negahban-Azar 2020).

After reviewing the current agricultural water reuse regulations and guidelines around the countries, Shoustarian and Negahban-Azar (2020) concluded that water quality parameters are generally divided into three categories: human-health parameters, agronomic parameters and physico-chemical parameters (Figure 3).

Figure 3. Water quality parameters. Source: Shoustarian and Negahban-Azar (2020)



Human health parameters are centred on safeguarding the health of farmers, local communities, workers and consumers and include microbiology parameters and chemicals (Shoushtarian and Negahban-Azar 2020). The microbiology parameters measure the presence of pathogens, with *E. coli* as the preferred faecal indicator. At the same time, chemicals refer to pharmaceuticals, personal care products and heavy metals (Shoushtarian and Negahban-Azar 2020). The pathogens' presence allows the assessment of the short-term biological risk of infection, while the chemical compounds evaluate the long-term biological risk of toxicity (Lazarova et al. 2004). The biological risks are commonly included in reclaimed water guidelines, but chemical risks are only included in a few water reclamation guidelines (Shoushtarian and Negahban-Azar 2020). The most common heavy metals included in irrigation water quality are arsenic (As), copper (Cu), chromium (Cr), cadmium (Cd), lead (Pb) and mercury (Hg) because they have shown health hazards when taken up by plants (Lazarova et al. 2004).Table 2 shows some of the most frequent chemicals and their regulatory limits in reclaimed water; the lowest concentrations are for Cd, Cr and As, while for Fe and Pd, values are higher.

Table 2. Chemicals and trace elements thresholds in agricultural water reuse regulations and guidelines. Source: Shoustarian and Negahban-Azar (2020)

Chemical/ trace element	Regulation (threshold as mg/L)		
	EPA	FAO	WHO
Arsenic (As)	0.1	0.1	0.1
Copper (Cu)	0.2	0.2	0.2
Chromium (Cr)	0.1	0.1	0.1
Lead (Pb)	5.0	5.0	-
Cadmium (Cd)	0.01	0.01	0.01
Nickel (Ni)	0.2	0.2	0.2
Iron (Fe)	5.0	5.0	5.0

Agronomic water quality parameters are more related with yield and quality of crops, maintenance of soil productivity and ecological health (Lazarova et al. 2004). Finally, the physico-chemical parameters are related with organic matter presence in water, total and dissolve solids that can cause clogging and corrosion in irrigation equipment and water turbidity, which reduce hydraulic conductivity and pollute soil surface (Shoushtarian and Negahban-Azar 2020).

2.4. Occupational health risks associated with wastewater treatment and reuse products

WHO (2006) defines a hazard as a "biological, chemical or physical constituent that can harm human health". Wastewater and sludge are sources of pathogenic organisms such as bacteria, viruses, parasitic protozoa and helminths, which comprise microbiological contaminants. So, exposure to untreated or not properly treated effluent and sludge through inhalation, ingestion or dermal contact can cause excreta-related diseases (WHO 2006). In addition, exposure to chemical constituents has been linked to cancer risk as a direct way of contamination, and these heavy metals and persistent organic pollutants (Dickin et al. 2016). Exposure groups are people prone to health hazards, for instance, sanitation workers, farmers, and local communities living around the land where wastewater or sludge is used (WHO 2016)

Consequently, WHO has published and updated guidelines since 1973 to protect and promote public health, emphasising exposure groups. Health risk management, health protection measures, and the assessment of risks (likely to be exposed to a hazard) are highlighted in the last edition (WHO 2016).

The hazards associated with using wastewater in agriculture are excreta-related pathogens that survive in the environment for a long time to cause diseases through exposure pathways such as contact with wastewater or sludge, consumption of contaminated crops, and drinking water from contaminated animals (Table 3). Aside from this, chemicals can also bioaccumulate in soil and plants, thus posing a health risk (Chaudhary et al. 2017).

It is important to note that the guidelines focus more on the short-term risks associated with pathogens and nutrients than the potential risk of heavy metals, pharmaceutically active compounds (PhAC) and endocrine-disrupting compounds (EDC) (Toze 2006). For instance, Table 3 designates the risk associated with heavy metals as low because their concentration in domestic water is low and conventional treatment removes it from the effluent and concentrates it in the sludge (Chen et al. 2013). However, heavy metals must be considered if the source of reclaimed water is industrial wastewater or if municipal and industrial wastewater is mixed (Toze 2006; Elgallal et al. 2016). Furthermore, this chemical contamination can be a concern in reclamation schemes in developing countries where industrial effluents enter domestic wastewater and natural water bodies (Qadir et al. 2010).

Table 3. Examples of hazards associated with wastewater use in agriculture. Source: (WHO 2016)

Hazard	**Exposure route**	**Relative importance**	**Comments**
Excreta-related pathogens			
Bacteria (*E. Coli, Vibrio cholerae, Salmonella ssp.*, *Shigella* ssp)	Contact Consumption	Low-high	Can survive in the environment long enough to pose health risks. Contamination of crops has led to disease outbreaks.
Helminths			
Soil-transmitted (*Ascaris*, hookworms, *Taenia* spp.)	Contact Consumption	Low-high	Present in areas where sanitation and hygiene standards are low. Eggs can survive for a very long time in the environment
Schistosomes (trematode bloodfukes)	Contact	Nil-high	Present only in certain geographic regions. Schistosomiasis is transmitted through contact with contaminated water in endemic areas

Protozoa (*Giardia intestinalis, Cryptosporidium Entamoeba* spp.)	Contact Consumption	Low-medium	Can survive in the environment long enough to pose health risks.
Viruses (hepatitis A virus, hepatitis E virus, adenovirus, rotavirus, norovirus)	Contact Consumption	Low-high	Can survive in the environment long enough to pose health risks. Contamination of crops has led to disease outbreaks.
Skin irritants	Contact	Medium-high	Skin disease such as contact dermatitis (eczema) have been reported after heavy contact with untreated wastewater.
Vector-borne pathogens (Plasmodium spp., dengue virus, *Wuchereria bancrofti,* Japanese encephalitis virus)	Vector contact	Nil-medium	Limited to geographic areas where the pathogen is endemic and suitable vectors are present.
Chemicals			
Heavy metals (arsenic, cadmium, lead, mercury)	Consumption	Low	Heavy metals may accumulate in some plants, but rarely to levels considered unsafe.
Halogenated hydrocarbons (dioxins, furans, PCBs)	Consumption	Low	Concentration of these substances is generally low in wastewater (but may be higher in sludge) These substances are usually adsorbed by soil particles and not taken up by plants.
Pesticides (aldrin, DDT)	Contact Consumption	Low	Risk is related to agricultural practices, wastewater generally does not contain high concentrations of these substances.

2.4.1. Sanitation Safety Plan (SSP)

Sanitation Safety Planning is a tool for sanitation systems that identifies and manages health risks in the sanitation chain. It guides the implementation of the 2006 WHO guidelines hence promoting improvements that target the most severe risks and reduce the health impacts of sanitation systems in the exposure groups (WHO 2006; Jackson and Vuong 2014).

An SSP must be implemented by: 1) Preparing the SSP area and team as well as stakeholder analysis; 2) describing the sanitation system, assessing the potential biological, physical, and chemical hazards, as well as the exposure group; 3) identifying the hazards, hazardous events, and exposure routes while determining the risk associated with the hazardous event, 5) developing and implementing an incremental improvement plan; 6) monitoring control measures, preparing review plans and supporting programs (Figure 4) (WHO 2022).

Figure 4. Modules of Sanitation Safety Planning (SSP). Source: (WHO, 2022)

SSP has been implemented in different countries; for instance, Jackson and Vuong (2014)reported a pilot test program in two locations in Hanoi, Vietnam: a composting plant and wastewater conveyance and agricultural use of wastewater without formal treatment. The study assessed the health hazards for farmers, consumers, and the local community in the first location and for workers in the second location. Similarly, Domini et al. (2017) executed an SSP for faecal sludge emptiers, workers in a co-composting plant, farmers reusing sludge and compost and local communities living near on-site sanitation systems, the co-composting plant and farms reusing sludge and compost. In contrast, a risk assessment methodology based on the SSP was developed to identify health risks related to workers in a WWTP in Iringa, Tanzania (Frattarola et al. 2019)and Kanpur, India (Babalola et al. 2023). Clavijo et al. (2020)executed a water and sanitation safety plan (WSSP) in Salta, Argentina, to evaluate the urban water cycle in the processes and sub-processes of the drinking water supply and sanitation system. All of these examples are related to microbial pathogens, but up to date, there has not been executed considering heavy metal hazards or chromium, as the present study is intended to explore.

2.4.2. Methods used for occupational risk assessment

According to the SSP guidelines, the risk assessment is the third step for executing an SSP. There are three different approaches to risk assessment: team-based descriptive decision, semi-quantitative risk assessment (SQRA) and Quantitative Microbial Risk Assessment (QMRA), or other quantitative methods (WHO 2016).

The team-based descriptive decision involves an agreement between the SSP team to classify the hazard as uncertain, low, medium or high while the semi-quantitative risks assessment uses a matrix to assign likelihood and severity to each hazardous event (WHO 2016). The semi-quantitative risk assessment is a more rigorous approach that works better in complex systems (WHO 2016). After describing the sanitation system and identifying the hazards, the SSP team assign a likelihood level (from 1: very unlikely to 5: almost certain) and a severity level (from 1: insignificant to 16: catastrophic) according to the correspondent description (Table 4) to each hazardous event to achieve a risk score and a risk level, as shown in Figure 5 (WHO 2016).

For example, (Mehmood et al. (2019)used quantitative methods to evaluate the health risk of cancer posed by chromium exposure in groundwater, surface water and wastewater in Faisalabad, Pakistan. Similarly, risks of human infection for Salmonella, rotavirus and protozoa (Giardia, Cryptosporidium) were assessed in six areas of willow coppice crops irrigated with wastewater along Sweden, Greece and Northern Ireland using a QMRA by (Carlander et al. 2009).

In particular, SQRA and some variations for risk assessments studies following the SSP were discussed in the previous section. For example, Jackson and Voung (2014) evaluated the risk in a team-based descriptive decision associating low, moderate and high levels to the hazardous events. Domini et al. (2017) used the matrix for SQRA and (Frattarola et al. 2019) combined the likelihood (Li) and severity (S) of a SQRA with a detectability factor (D) related to O&M of the treatment steps in the WWTP. The integrated approach of Clavijo et al (2020) assessed the risks through probability and severity values of a modified scale for the processes of water and sanitation systems in Salta, Argentina.

Table 4. Description for classification of likelihood and severity in a SQRA (source: WHO, 2016)

Descriptor		Description
Likelihood (L)		
1	Very unlikely	It has not happened in the past, and it is **highly improbable** it will happen in the next 12 months (or another reasonable period).
2	Unlikely	It has not happened in the past but **may occur in exceptional circumstances** in the next 12 months (or another reasonable period).
3	Possible	It May have happened in the past and **may occur under regular circumstances** in the next 12 months (or another reasonable period)
4	Likely	It has happened in the past and **is likely to occur** in the next 12 months (or another reasonable period)
5	Almost certain	It has happened in the past and **will almost certainly occur** in the next 12 months (or another reasonable period)
Severity (S)		
1	Insignificant	Hazard or hazardous event resulting in **no or negligible health effects** compared to background levels.
2	Minor	Hazard or hazardous event potentially resulting in **minor health effects** (e.g. temporary symptoms like irritation, nausea, headache)
3	Moderate	Hazard or hazardous event potentially resulting in **self-limiting health effects or minor illness** (e.g. acute diarrhoea, vomiting, upper respiratory tract infection, minor trauma).
4	Major	Hazard or hazardous event potentially resulting in **illness or injury** (e.g. malaria, schistosomiasis, food-borne trematodiases, chronic diarrhoea, chronic respiratory problems, neurological disorders, bone fracture); and may lead to a legal complaint; and or significant regulatory non-compliance
5	Catastrophic	Hazard or hazardous event potentially resulting in **serious illness or injury, or even loss of life** (e.g. severe poisoning, loss of extremities, severe burns, drowning); and will likely lead to a significant investigation by a regulator with a prosecution

Figure 5. Matrix for semiquantitative risk assessment. Source: (WHO, 2016)

			SEVERITY (S)				
			Insignificant	Minor	Moderate	Major	Catastrophic
			1	2	4	8	16
LIKELIHOOD (L)	Very unlikely	1	1	2	4	8	16
	Unlikely	2	2	4	8	16	32
	Possible	3	3	6	12	24	48
	Likely	4	4	8	16	32	64
	Almost certain	5	5	10	20	40	80

Risk score R = L × S	<6	6–12	13–32	>32
Risk level	Low risk	Medium risk	High risk	Very high risk

Furthermore, in the review of health risks associated with wastewater irrigation, Dickin et al. (2016) noted that few studies assess chemical exposure to wastewater use compared to microbiological hazards. The authors stated that there is still a gap in assessing exposure to chemicals in communities with wastewater reuse considering the emerging contaminants produced by industrial sectors in Southeast Asia and Sub-Saharan Africa (Dickin et al. 2016).

2.5 Wastewater treatment and reuse in India

Despite the multiple campaigns in India to address open defecation and promote sanitation, cleanliness and toilet coverage, Wankhade (2015) emphasizes that around 60 million people in urban areas lack improved sanitation, and 67% of the wastewater is discharged to the environment without treatment. Besides, it is crucial to expand the attention to the whole sanitation service chain comprising conveyance and treatment, but also in on-site systems and O&M to improve sanitation (Wankhade 2015). To promote sanitation, the government of India has initiated programmes to improve sewered and un-sewered sanitation, such as Swacch Bharat Mission, AMRUT Mission and Smart City initiative (Cuadrado-Quesada et al. 2020). In addition, the Namami Gange project aims to clean the River Ganga and abate pollution (Breitenmoser et al. 2022).

According to the Central Pollution Control Board (CPCB) (2021a), the sewage generation in India is around 72,368 MLD, and the installed treatment capacity covers only 43.9%. In addition, only 60% of the wastewater the industries generate is treated and disposed of in rivers (CPCB 2021a). From industries in India, there are around 1000 Grossly Polluting Industries (GPIs) located in the river Ganga main stem, of which 84% are located in the state of Uttar Pradesh, and the main industrial activities are tanneries (400), textile (188), sugar (107) and distillery (55) (CPCB 2021b). Also, most of the wastewater irrigation schemes in the country are located along the rivers near developing cities such as Delhi, Kolkata, Coimbatore, Hyderabad, Indore, Kanpur, Patna, Vadodara, and Varanasi (Hoek 2004). In most cities, the same sewerage system receives domestic and industrial wastewater, which affects the composition of the wastewater and consequently increases the concentrations of toxic chemicals and heavy metals (Minhas et al. 2022).

2.5.1 Wastewater treatment in India

The actual utilized capacity of STPs in India only covers 27.9% of the total wastewater generation (CPCB 2021a). Furthermore, out of this 27.9%, only 23% of the treatment capacity meets the standards of the State Pollution Control Boards (SPCBs) (CPCB 2021a). So, there is a gap of 72.1% in wastewater treatment capacity and compliance with the SPCBs (CPCB 2021a).

By 2021, 1469 STPs were installed in the country (CPCB 2021a). The most common secondary treatment technologies (Section 2.2) installed are sequential batch reactor (SBR) (33%) followed by activated sludge process (ASP) (21%) and Upflow-Anaerobic Sludge Blanket (UASB) (4.7%) (CPCB 2021a). Natural treatment systems are also utilized, for example, waste stabilization ponds and oxidation ponds(CPCB 2021a). Most STPs are in cities with high industrial activities(Minhas et al. 2022).

Industries must also comply with discharge standards by using individual effluent treatment plants. However, for small to medium industries, common effluent treatment plants (CETPs) collectively treat effluent at a single site (Padalkar and Kumar 2018). The main advantages of CETPs are the sharing expenses, treatment of heterogeneous effluent in an industrial cluster and easy operation and maintenance (Padalkar and Kumar 2018; Ghumra et al. 2021). Around 193 CETPs are installed in India comprising primary, secondary biological treatment and tertiary treatment (Ali et al. 2021). Yet, the varying incoming effluent quantities and qualities from the industries present a challenge that has made the performance of CETPs in India deficient (Ghumra et al. 2021).

In the case of tanning (preserving animal hides to produce leather), India has a historical practice (Chaudhary et al. 2017). The leather industry is distributed in Tamil Nadu, Uttar Pradesh, Andhra Pradesh, West Bengal, Karnataka, Maharashtra and Punjab. It is estimated that the effluent discharge is approximately 50,000 m^3/day, which, together with the toxic chemicals (section 2.5.5) used during tanning, threatens the local community (Chaudhary et al. 2017). The principal pollutants produced by the leather industry are chromium, tannins, sulphides and other chemical compounds containing dyes, ammonium salts, acids, and other heavy metals such as zinc (Zn), copper (Cu), lead (Pb) and cadmium (Cd) (Chaudhary et al. 2017).

2.5.2 Wastewater products and their reuse in India

In India, the concept of water reuse is not something new, as revealed by the first reported case of this process in 1964 and the use of wastewater for irrigation since 1970 (Goyal and Kumar

2021). However, due to water stress, wastewater reuse is a feasible alternative in India to achieve a sustainable water future and face a water crisis (CPHEEO 2021).

CPHEEO (2021) states that 32 of 54 cities with more than 1 million population have adopted reuse projects, and 17% of the wastewater generated from the cities is being recycled and reused (CPHEEO 2021). For instance, reclaimed water is used for horticulture and agriculture in Kanpur, Uttar Pradesh and industrial cooling in Maharashtra, Nagpur and Chennai, Tamil Nadu (CPHEEO 2021). However, untreated or partially treated sewage is common in the country due to the lack of fresh water (Breitenmoser et al. 2022).

2.5.3 National standards for effluent and sludge

The Indian Ministry of Environment Forest and Climate Change (MoEFCC) issued in 1986 the minimum wastewater discharge standards (Table 5), required for all states in India, including suspended solids, pH, BOD, COD, nitrogen concentrations and heavy metals (MoEFCC 1986). The maximum limit for total Cr is 2.0 mg/L (Table 5) when discharging in inland surface water, public sewers and marine coastal areas; meanwhile, for hexavalent chromium, the maximum limit for discharging in inland surface water is 0.1mg/L, principally to its carcinogenic effect (Section 2.5.6). In addition, the Central Public Health and Environmental Engineering Organisation (CPHEE) prescribed standards for reusing treated sewage, as shown in Table 6 but it does not include parameters for heavy metals (CPHEEO 2013). Toxic effects are only considered in terms of plant growth, and for this purpose, CPHEEO established some maximum permissible concentrations of elements in irrigation water regarding the type of soil (Table 7) (CPHEEO 2013).

Table 5. General standards for discharge of environmental pollutants for effluents. Values in mg/L unless stated. Source: (MoEFCC 1986)

No	Characteristics	Standards			
		Inland Surface Water	Public Sewers, (A)	Land for Irrigation	Marine Coastal Areas
1	Colour and odour	(B)		(B)	(B)
2	SS	100	600	200	(C), (D)
3	Particle size of SS	(E)	-	-	(F), (G)
4	pH value	5.5 to 9.0			
5	Temperature	(H)	-	-	(H)
6	Oil and grease	10	20	10	10
7	Total residual chlorine	1.0	-	-	1.0
8	Ammoniacal nitrogen (as N)	50	50	-	50
9	Total Kjeldahl Nitrogen, (TKN) (as N)	100	-	-	100
10	Free ammonia (as NH_3)	5.0	-	-	5.0
11	Biochemical Oxygen Demand	30	350	100	100
12	Chemical Oxygen Demand	250	-	-	250
13	Arsenic (as As)	0.2			
14	Mercury (as Hg)	0.01	0.01	-	0.01
15	Lead (as Pb)	0.1	1.0	-	2.0
16	Cadmium (as Cd)	2.0	1.0	-	2.0
17	Hexavalent Chromium (as Cr 6+)	0.1	2.0	-	1.0
18	Total Chromium (as Cr)	2.0	2.0	-	2.0
19	Copper (as Cu)	3.0	3.0	-	3.0
20	Zinc (as Zn)	5.0	15.0	-	15.0
21	Selenium (as Se)	0.05	0.05	-	0.05
22	Nickel (as Ni)	3.0	3.0	-	5.0
23	Cyanide (as CN)	0.2	2.0	0.2	0.2
24	Fluoride (as F)	2.0	15.0	-	15.0
25	Dissolved phosphates (as P)	5.0	-	-	-
26	Sulphide (as S)	2.0	-	-	5.0

Table 6. Recommended norms of treated sewage quality for specified activities at point of use. Source: (CPHEEO 2013)

S1. No.	Parameter	Landscaping, Horticulture & Agriculture			
		Horticulture, Golf course	Crops		
			Non edible crops	crops which are eaten	
				Raw	Cooked
1	Turbidity (NTU)	<2	AA	<2	AA
2	SS	nil	30	nil	30
3	TDS	2100			
4	pH	6.5 to 8.3			
5	Temperature °C	Ambient			
6	Oil & Grease	10	10	nil	nil
7	Minimum Residual Chlorine	1	nil	nil	nil
8	Total Kjeldahl Nitrogen as N	10	10	10	10
9	BOD	10	20	10	20
10	COD	AA	30	AA	AA
11	Dissolved Phosphorous as P	2	5	2	5
12	Nitrate Nitrogen as N	10	10	10	10
13	Faecal Coliform in 100 ml	nil	230	nil	230
14	Helminthic Eggs/ litre	AA	<1	<1	<1
15	Colour	Colourless		Colourless	Colourless
16	Odour	Aseptic which means not septic and no foul odour			

All units in mg/l unless specified; AA-as arising when other parameters are satisfied; A tolerance of plus 5% is allowable when yearly average values are considered.

Table 7. Maximum permissible concentration of toxic elements in irrigation waters. Source (CPHEEO 2013)

Element		Maximum permissible concentration (mg/l)	
		On all soils in continuous use or acidic soils	For short term use of textured alkaline soils
Aluminium	Al	1.0	20.0
Arsenic	As	0.1	2.0
Beryllium	Be	0.1	0.5
Boron	B	0.5	1.0
Cadmium	Cd	0.01	0.05
Chromium	Cr	0.10	1.0
Cobalt	Co	0.05	5.0
Copper	Cu	0.2	5.0
Iron	Fe	5.0	20.0
Lead	Pb	5.0	10.0
Lithium	Li	2.5	2.5
Manganese	Mn	0.20	10.0
Molybdenum	Mo	0.01	0.01
Nickel	Ni	0.20	2.0
Selenium	Se	0.005	0.01
Vanadium	V	0.10	1.0
Zinc	Zn	2.0	10.0

2.5.4 Risk assessment in wastewater reuse

Considering the wastewater products and the reuse in India mentioned in section 2.5.2, assessing the health risks (section 2.4) associated with this planned wastewater reuse scheme is crucial. Some examples of earlier risk assessment studies in India will be presented.

For instance, the risk of intestinal nematode infection associated with wastewater use in agriculture was assessed in farming families in Hyderabad, India, by Ensink et al. (2008). The method used included the association between water quality in three zones of Hyderabad and intestinal infection by identifying nematodes ova (Ensink et al. 2008). They found that the risk of hookworm and *Trichuris trichiura* was higher when untreated wastewater was used rather than partially treated wastewater, which was only associated with Ascaris lumbricoides infection risk.

Rattan et al. (2005) assessed the effect of long-term irrigation with reclaimed water on metal content in soils and plants and the risk of consuming vegetables grown in these conditions in peri-urban areas of Delhi, India, under the Keshopur Effluent Irrigation Scheme (KEIS). The risk assessment was based on the hazard quotient for intake of Zn, Cu and Ni (Rattan et al. 2005). They found that iron concentration in soil was affected by irrigation with sewage for five years, but after irrigating with sewage for 20, there was a build-up of Zn, Cu, Fe, Ni and Pb (Rattan et al. 2005).

Regarding occupational health in the wastewater treatment plants, Babalola et al. (2023) explore the impact of the implementation of novel technology and the associated risks for STP workers and farmers reusing the effluent in Kanpur, Uttar Pradesh, through a semi-quantitative risk matrix assessment. The study was focused on microbiological risks and found that the levels of E. coli in the effluent at the STP were high, and the impact of the novel technology implied that the number of health risks for the STP workers increased, but the severity of the risks would decrease (Babalola et al. 2023). For the farmers reusing the treated effluent of the STP, the number and severity of risks would decrease due to the improvement in effluent quality if the novel technology were implemented (Babalola et al. 2023).

2.5.5 Common pollutants from tanneries

The Tannery sector contributes to around 58% of the industrial pollution in India, and 66% of the industries are located along the river Ganga (Dwivedi et al. 2018). The transformations involved in leather production consume high quantities of water that is then discarded as a complex mixture of pollutants (Oller et al. 2011). The tanning effluents contain sulphuric acid, chrome, chlorides, sodium bicarbonate and sulphates (Chowdhury et al. 2015).

Chromium salts are widely used during chrome tanning, which is used in 90% of the world's leather produced (Chaudhary et al. 2017). In particular, the tanning agent is basic chromium (III) sulfate (BCS), which forms a complex with the collagen component of the leather to create a layer that protects leather pores from putrefaction (Fabiani et al. 1997). Due to the significant amount used and its toxicity, chromium waste from tanneries is a source of environmental pollution and health concern (Kokkinos et al. 2019). For instance, 2000-3000 tons of chromium are released into the environment in India, with chromium concentrations between 2000 to 5000 mg/L in the effluent (Sugasini and Rajagopal 2015). Approximately 40% of the initial amount of trivalent chromium remains in the wastewater and sludge. Kokkinos et al. (2019) state that hexavalent chromium in tannery sludge "barely exists" but Ramteke et al. (2010) suggest that chromium remaining in the wastewater can be oxidized to hexavalent chromium during the treatment process.

Chromium is an element present in the Earth's crust in different oxidation states, from -2 to +6, but the most common species are trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] (Sun and Costa 2022). Trivalent chromium exists in water as $Cr(H_2O)OH^{2+}$ and forms insoluble complexes and precipitates as hydroxide, oxide and sulphate, or it is adsorbed on the colloidal matter (Gomez and Callao 2006; Ahemad 2014). On the other hand, hexavalent chromium is highly soluble in water and is present as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$) and hydrochromate ($HCrO_4^-$) (Cheremisinoff and Rosenfeld 2010). Cr(VI) can persist as soluble complex anions in aquatic media or react with organic matter to form Cr(III) species (Ramteke et al. 2010).

2.5.6 Health hazards related to chromium

Of the two common species of chromium, trivalent chromium has not been considered toxic, but hexavalent chromium has been included in the top 20 of the Substance Priority List of the Agency for Toxic Substances and Diseases Registry (ATSDR), determined to pose a potential threat to human health due to its toxicity (ATSDR 2022). Hexavalent chromium is carcinogenic and poisonous (ATSDR 2012; Georgaki and Charalambous 2022).

The general population is exposed to chromium (as trivalent chromium, generally) levels from air, water and food in the ranges of 0.2- 0.4 μg, 2.0 μg and 60 μg, respectively (U.S. EPA 2000). Occupational exposure can be two orders of magnitude higher (U.S. EPA 2000). Cheremisinoff and Rosenfeld (2010) stated that occupational exposure has been studied in several industries, such as chromate production, chrome-plating, chrome pigment, gold mining and leather tanning. The stainless-steel welding, carbon steel welding, and painting industries have the most significant proportion of workers exposed to Cr(VI) (Sun and Costa 2022).

The main exposure pathways to chromium are ingestion, inhalation and skin contact; the last two are occupational exposure (Cheremisinoff and Rosenfeld 2010; Shin et al. 2023). Cr(VI) can cause allergic dermatitis, skin and nasal irritation, and ulceration when in contact with humans. Furthermore, due to its membrane permeability, it can enter the cell and cause oxidation processes to DNA, leading to carcinogenic effects and health hazards such as lung carcinoma, renal tubular necrosis and respiratory tract cancer (Chaudhary et al. 2017).

Through inhalation pathways, workers exposed to chromium-containing dust and mist experience respiratory issues such as nose irritation and breathing problems such as asthma, cough and wheezing (Cheremisinoff and Rosenfeld 2010; ATSDR 2012). The limits of hexavalent chromium and trivalent chromium set by OSHA (Occupational Safety and Health

Administration) in the air are 0.005 mg/m^3 and 0.5 mg/m^3 for a work day of 8 hours (ATSDR 2012). The difference between hexavalent and trivalent chromium limits is related to the slow rate at which trivalent chromium is absorbed (U.S. EPA 1998). EPA also set a maximum contaminant level for total chromium in drinking water of 100 µg/L (ATSDR 2012).

Through skin contact, workers can develop allergies and skin rashes with pain and itching (ATSDR 2012). Trivalent chromium is also allergenic but to a lesser degree than hexavalent chromium (Baruthio 1992).

For instance, trivalent chromium salts combine with the proteins after penetrating the skin to form complexes, while hexavalent chromium can move through the body and cross cell membranes (Baruthio 1992). However, a high concentration of trivalent chromium can induce sensitization, which means reverse tolerance to allergies (Baruthio 1992).

The main problems of chromium-compounds ingestion, especially hexavalent chromium, involve stomach irritation, ulcers and anemia (ATSDR 2012). Hexavalent chromium also affects the liver, kidney, immune and gastrointestinal system (U.S. EPA 2000).

Trivalent chromium has been considered an essential nutrient by the Institute of Medicine of the National Research Council, and the adequate intake is between 20-45 µg of trivalent chromium per day for adolescents and adults (ATSDR 2012). This information has been mentioned in several studies considering the toxicology of chromium compounds (U.S. EPA 1998, 2000; Flora 2014; Georgaki and Charalambous 2022). The biological effects of trivalent chromium are related to glucose tolerance, oxidation and uptake (Georgaki and Charalambous 2022). However, adverse effects in case studies of humans using high-dose trivalent chromium compounds as dietary supplements (ATSDR 2012). Acute animal tests showed moderate toxicity from oral exposure to trivalent chromium (U.S. EPA 2000). In addition, (Aharchaou et al. 2022a) pointed out the increasing evidence of trivalent chromium adverse effects in terrestrial and aquatic organisms. In vitro studies have shown that trivalent chromium can cause DNA damage, but to a lesser degree than hexavalent chromium, due to its inability to cross cell membranes (Monga et al. 2022). However, hexavalent chromium and trivalent chromium can produce free radicals/reactive oxygen species, which are involved in cancer development (Monga et al. 2022).

Chapter 3. Research methodology

This chapter present the proposed approach to achieve the research objectives. It presents the research design and explain the executed data collection methods.

3.1. Study background

This study is part of the Pavitra Ganga project, a research and innovation initiative from the European Union/ India cooperation, that aims to tackle the pollution of the Ganga River through the implementation of innovative wastewater treatment technologies and resource recovery opportunities at Kanpur and Barapullah, New Delhi (Horizon 2020) . The main objective is to achieve the clean water and sanitation (SDG 6) for urban and peri-urban areas in India by unlocking the potential of wastewater treatment and reuse. The three pillars of the project are: 1) people: creation of participatory approach, providing treatment solutions for open drains; 2) planet: rejuvenation of the River Ganga through improvement of effluent water quality; 3) profit: exploring resource recovery and opportunities of waste-to-energy (Pavitra Ganga 2020).

3.2. Case study area

Kanpur, (26° 26’ 59.7228’’ N, 80° 19’ 54.7464’’ E) is the biggest city of the state Uttar Pradesh, located on the southern bank of the Ganga River and also known as the industrial and commercial capital the state. It is situated along national highways No 2 and 25, as well as a state highway. In addition, it is located along the main railway trunk line connecting Delhi and Howrah (JPS Associates LTD 2006). It is popular for its leather industry and contributes with around 13.5% of the country’s leather exports (JPS Associates LTD 2006). The climate can be divided in four seasons: summer (March to June) with temperatures above 41 °C; south-west monsoon (July to September) with temperatures around 27-35 and 90% of the precipitations (450-750 mm); post-monsoon or transition period (October to November) and cold season (November to February) with temperatures of 4-8 °C (JPS Associates LTD 2006; Bassi et al. 2019).

The population has increased three times in the last three decades, up to 2.9 million in the Census of India 2011 (Bassi et al. 2019). The decadal growth rate of the city is 8.9%, and the average density of the city is 11,583.43 persons/km^2. Kanpur Municipal Corporation (KMC) is the urban local body. The city has nine zones and 110 election wards (Apurva 2020).

In a brief overview of assessing the urban sanitation service of the city, the SFD shows that the most critical areas are the sewerage network, with an efficiency of 38.4% (Figure 6). Other issues are related to septic tanks connected to open drains (15% of the population) and fully lined tanks connected to open drains (23%) (Apurva 2020).

The city has districts completely sewered as Nawab Ganj, Cantonment, Jajmau, Sanigawan, Sajari, Chakeri, and Mathurapur; meanwhile, there are areas answered such as Kalyanpur, Armapur, Defence Colony (Apurva 2020). There are four operational wastewater treatment plants STPs in Kanpur City (Table 8), three of them are STP and one is the CETP. Two STP and the CETP are located in the same facility near the tanneries in Jajmau (Bassi 2019). Considering the operational capacity of the STPs, Apurva (2020) states that the total operational in the city is 80%. However, Bassi (2019) suggests that the actual treatment is less due to operational constraints, so only 27% of the wastewater generated is treated.

Figure 6. SFD of Kanpur. Source: (Apurva 2020)

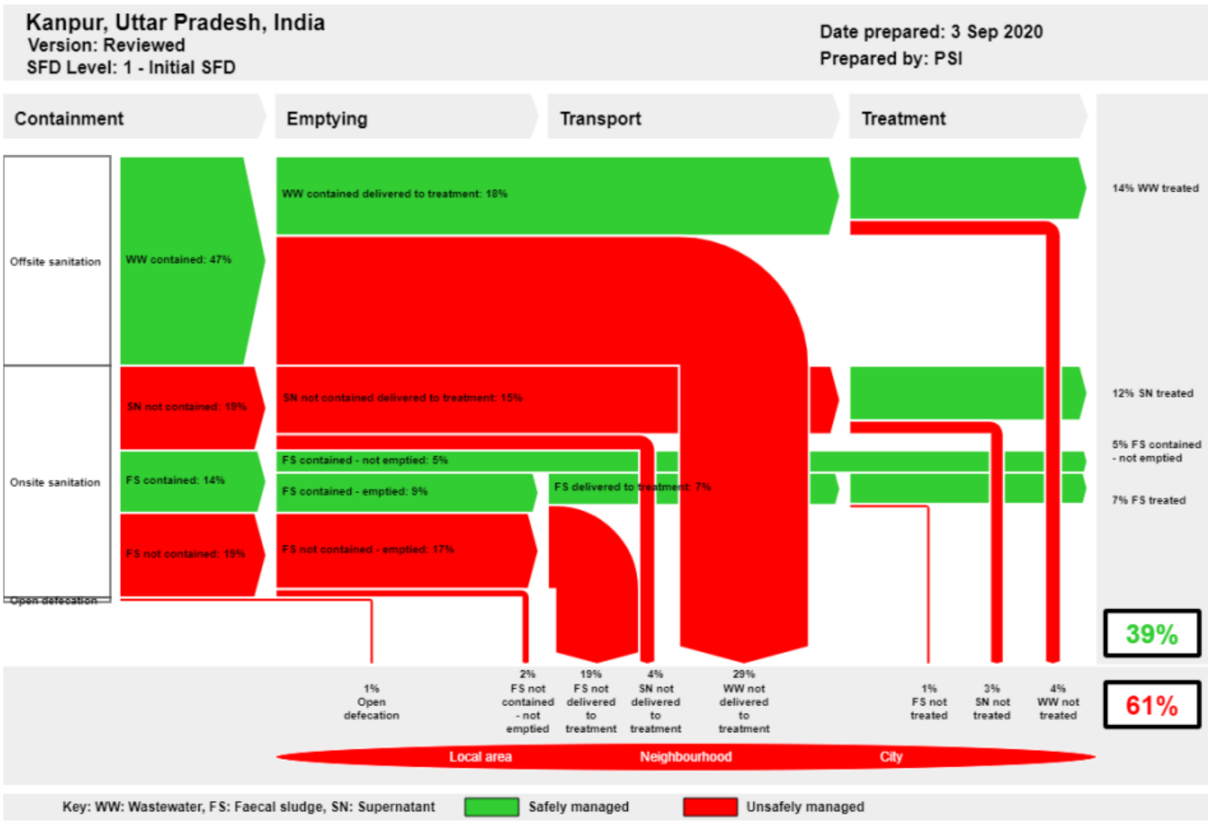


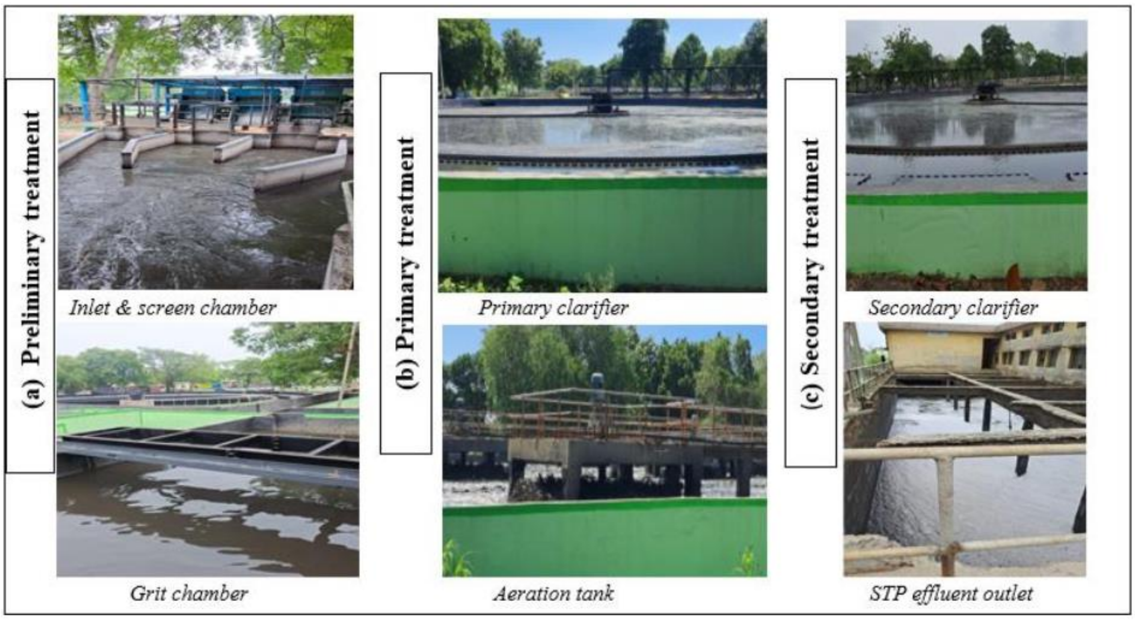
Table 8. Details of sewerage treatment plants in Kanpur city. Source: (Bassi et al. 2019)

Location of STP/CETP	Year of commissioning	Technology used	Type of waste water fed	Installed capacity (MLD)	Actual treatment (MLD)	Use of treated water
Jajmau	1989	Up flow Anaerobic Sludge Blanket (UASB)	Domestic	5	4.5	Treated effluent flows into river Ganges
Jajmau	1994	UASB	Domestic and industrial	36	19	Treated effluent irrigates 2200 ha of sewerage farm. Untreated wastewater is discharged into the river Ganges
Jajmau	1999	Activated Sludge Process (ASP)	Domestic	130	100	
Bingawan	2014	UASB	Domestic	210	65.5	Untreated wastewater is discharged into the river Ganges

3.3. Research focus area

This study is focused on the 130 MLD STP at Jajmau which uses ASP as its secondary treatment process (Table 8). The STP was commissioned in 1999, and though its installed capacity is 130 MLD (Table 8), the actual utilization is around 100 MLD (CPCB 2021a). Illegal discharges from tanneries have reached the Jajmau STP since its commission and have affected the STP's performance (JNNURM 2006). The treatment train entails a screen, primary clarifier, surface aeration tank, and secondary clarifier (Figure 7) (Babalola 2022). The study also stated that there is no further disinfection after secondary clarifying and that the sludge generated from the STP is disposed of in a landfill due to its chromium toxicity. However, there is no information about the sludge management steps in the STP (Babalola 2022).

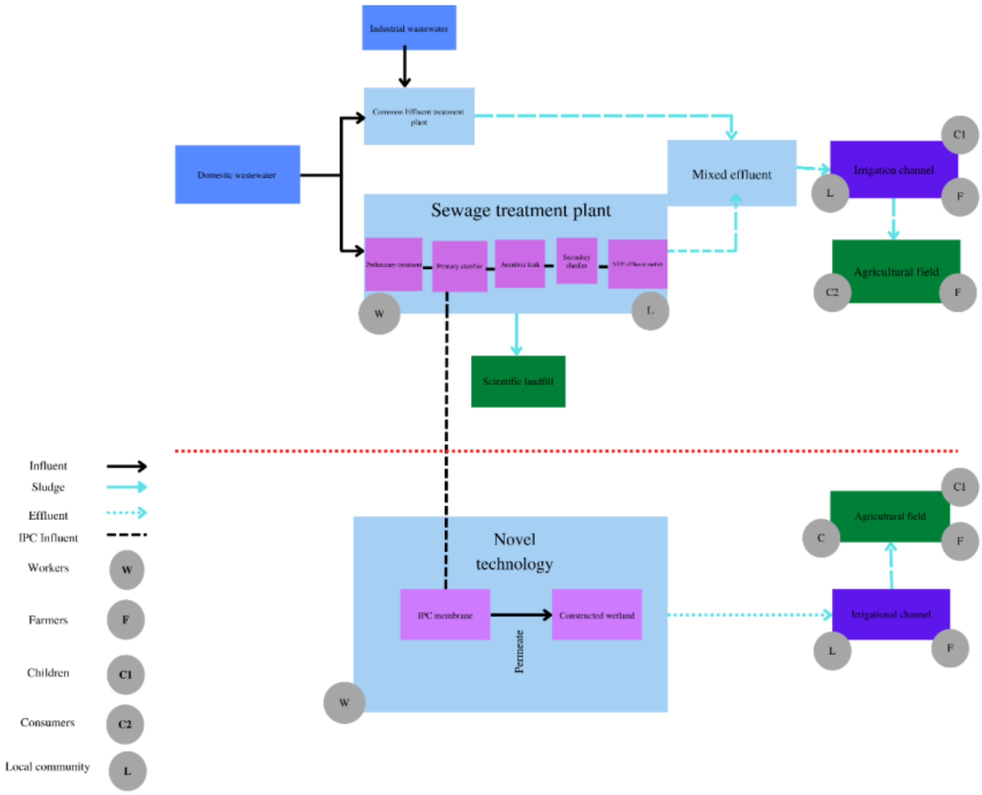
Figure 7. Treatment train of the 130 MLD STP. Source: (Babalola 2022)



The novel technology comprises an integrated permeate channel (IPC) – membrane and a constructed wetland plus (CW+). The IPC membrane is an integrated permeate channel that combines the conventional activated treatment with filtration at low pressure (Ion Exchange India). One of the main advantages is the reduction in sludge generation, so less sludge handling is required (Ion Exchange India). The IPC pilot implemented by Pavitra Ganga had been operating for less than one month when the present study was executed, so there was not enough sludge between the membrane plates to sample. However, the pilot proposes to treat the generated sludge of the IPC through anaerobic digestion, which has not been implemented to date.

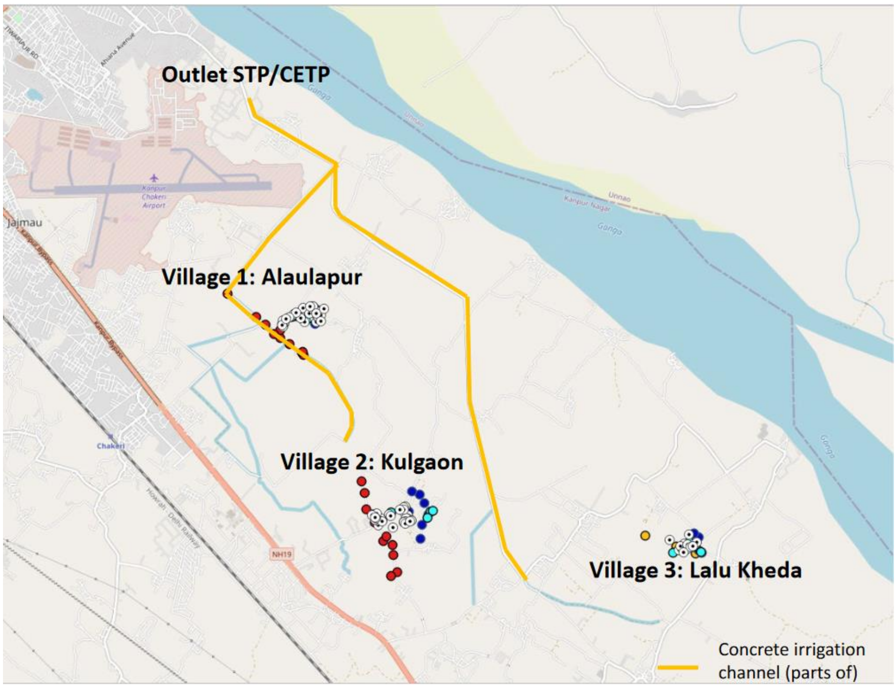
The effluent from the primary clarifier is the influent of this technology. After the IPC, the effluent goes to the CW+, a shallow basin filled with filter material like sand or gravel and planted with vegetation tolerant to saturated conditions (UN-HABITAT 2008). The CW+ pilot was designed to remove micro-pollutants and pathogens but also contains specific sorbents for removing heavy metals (Pavitra Ganga Project; Babalola et al. 2023). These sorbents are mainly granular activated carbon (GAC), zeolites and $CaCO3$ (Pavitra Ganga Project). The process flow for wastewater safety planning in the case study was proposed by Babalola (2022) and indicated the conventional treatment train in the STP and the integration of the novel technology pilot and the exposure group in the analysed system (Figure 8).

Figure 8. Process flow for wastewater safety planning in Kanpur. Source (Babalola 2022)



The effluent of the 130 MLD STP is then mixed with the effluent of the 36 MLD CETP and pumped to a concrete irrigation channel that supplies irrigation water to 2,200 ha of farmland in the nearby villages (Figure 9) (JNNURM 2006; Breitenmoser et al. 2022). From Alaulapur and Kulgaon villages, 180 households and 450 households, respectively, receive water from the mixed effluent and use it for flood/furrow irrigation farming of rice, wheat and millet (Breitenmoser 2022). The wastewater reuse scheme in Kanpur is driven by water scarcity, and though it seems to meet some criteria of irrigation types (Table 1), such as management status, official recognition and direct use, it still lacks in health risk mitigation focus and water quality. Regarding the latter, earlier studies have mentioned that the poor quality of the mixed effluent has decreased crop yields, polluted the groundwater and increased stomach and skin-related problems (Singh 2006; Cuadrado-Quesada et al. 2020).

Figure 9. Location of villages Alaulapur and Kulgaon, reusing the mixed effluent STP + CETP. Source: (Breitenmoser 2022)



3.4. Research design/ approach

The study is proposed to have a mixed methods approach, which combines quantitative and qualitative data in tandem to enhance the understanding of the information and make statistical inferences, focusing on answer the research questions(Creswell 2003).

The total Cr and Cr(VI) determination will generate quantitative data to achieve the first objective. The mass balance approach requires not only chromium concentrations but also secondary information from reports and process STP information data as well as key informant interviews. For the third and fourth objectives, it is necessary to gain information about the STP activities and exposure as well as structured observation and key informant interview for the implementation of a semi-quantitative risk assessment related to chromium levels along the STP for the STP workers regarding the conventional treatment train and the novel technologies. The data collection methods will be described in the following section.

3.5. Data collection methods

3.5.1. Secondary data collection

The secondary data comprised information about the Pavitra Ganga project and the innovation site as well as journal articles, manuals, reports related with the study. The data obtained was related to the STP conventional technology processes as well as the novel technology, maximum parameters related to irrigation water quality from government reports such as CPCB, and relevant information regarding the procedures and methods for chromium determination.

For the risk assessment, the secondary data entails the hazardous events and exposure groups identified by Babalola (2022) in the STP as well as health hazards related to chromium in a wastewater reuse scheme.

3.5.2. Primary data collection

Key Informant Interview (KIIs)

The KIIs were conducted to obtain primary data from stakeholders for achieving the research objectives 1 and 3. The interview questionnaires were prepared before the interviews using a semi-structured approach. The interviews were face-to-face and notetaking was used to collect the information. After that, data was summarized and analysed. Table 9 shows the codes adopted for key informants. Data obtained from these sources aimed to expand the process mapping studied by Babalola (2023) to include sludge management practices in the research focus areas as well as to obtained information about process flow rates and sludge fate, volumes or quantities for the mass balance of chromium (Objective 2), and finally for the risk assessment (objective 3 and 4)

Table 9. Codes implemented for key informants

Context	Location	Designation	Number of participants	Codes
STP	130 MLD STP Jajmau	Manager and worker	2	K-01 to K-02
Novel technologies	IPC CW+	Technology operators	2	K-03 to K-04

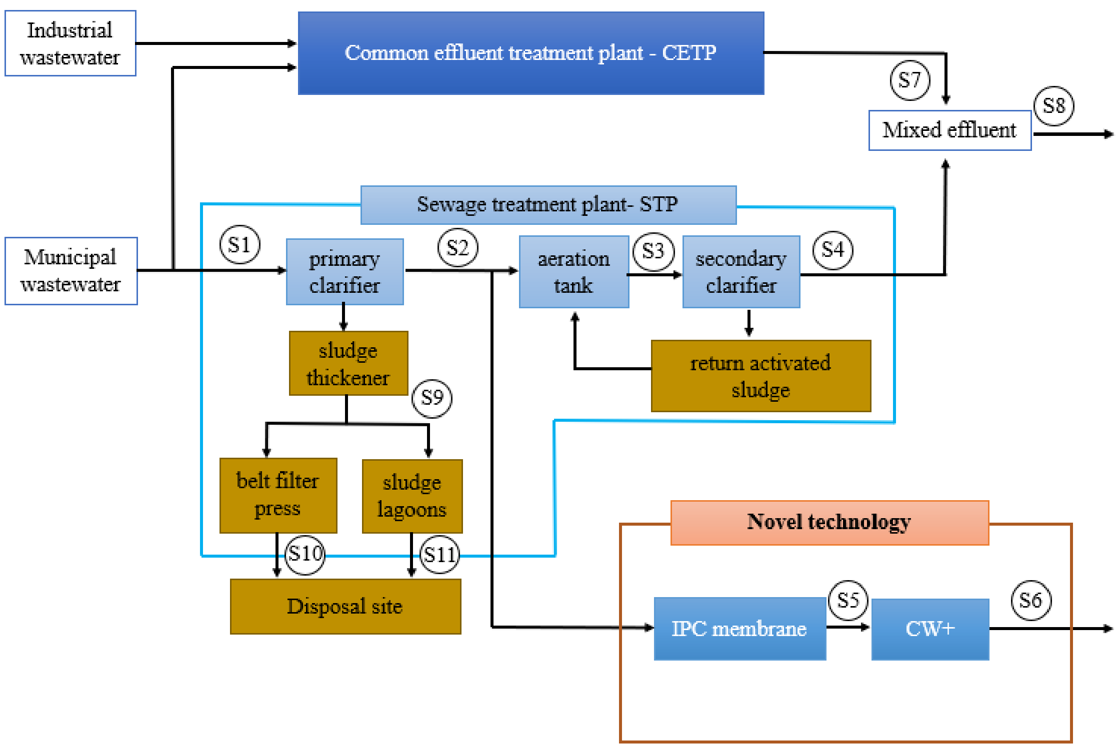
Structured observation

This method aimed to obtain information during the field visits related to the study area such as the treatment steps in the STP, the sludge management in the STP and the fate of sludge, the hazardous events and exposure pathways to triangulate the information with the previous study of SSP executed by Babalola (2022). The executed method involved paying attention to work practices in the STP, taking notes and photographs.

Total Cr and Cr(VI)

Sampling strategy: The sampling points along the treatment train are displayed in Figure 10. In addition, Table 10 describes the sampling points, the type of sample, and the number of samples taken per point per campaign. The type of samples was time composite to represent the average wastewater characteristics, taken at intervals of two hours during the operation hours of the STP Jajmau. During the three campaigns, sixty-six composite samples were obtained in duplicate (total= 132). All samples were taken between July and August 2023, during the monsoon season. In addition, during the third campaign, four additional grab samples were taken from the STP influent to analyse the Cr variation during the different intervals. Each composite sample was collected in a 250 mL container and transported to the laboratory in a cooled box to keep the temperature at ≤ 6ºC. After that, it was acid-preserved with nitric acid for further digestion in the case of total Cr determination. It was then analysed within the first 24 hours for Cr (VI) determination.

Figure 10. Sampling points in the STP Jajmau



Initially, there were fourteen proposed sampling points, but three of them could not be sampled due to the following reasons: firstly, the current treatment is recycling all the activated sludge from the aeration tank, so there is no waste activated sludge; secondly, during the time that the campaign was executed, the IPC pilot had not collected enough sludge in the membranes; and finally, no sample was taken from the constructed wetlands.

Table 10. Description of sampling points and type of sample

No SP	Name	Description of the sampling point (SP)	No of samples total Cr/campaign	No of Samples Cr (VI)/campaign
S1	IN	Plant influent	2	2
S2	CL1	Effluent of primary clarifier Influent of IPC (novel techn)	2	2
S3	AT	Effluent of aeration tank	2	2
S4	CL2	Effluent of secondary clarifier	2	2
S5	IPC	Effluent of IPC	2	2
S6	CW+	Effluent of CW+	2	2
S7	CETP	Effluent STP+CETP	2	2
S8	STP+CETP	Combined effluent STP+CETP	2	2
S9	SL-TH	Sludge after thickening	2	2
S10	SL-MDW	Waste activated sludge (and/or)	2	2
S11	SL-LG	Return activated sludge	2	2

Determination of total Cr and Cr(VI)

The determination of chromium was made for total chromium and hexavalent chromium in order to explore the speciation of chromium in wastewater and sludge (objectives 1 and 2). The sample preparation guidelines are described in the EPA methods SW-846 Method 3060A and SW-846 Test Method 6020B (Baird and Bridgewater 2017)The Cr determination was made using two methods: no digestion and digestion. From the chemical analytical perspective, the digestion is made for samples containing particulates or organic materials, and its main objective is the chemical degradation of the sample matrix (Baird and Bridgewater 2017). This process reduces the interferences of organic matter and converts the metals bounded to particulate matter to its free form (Baird and Bridgewater 2017). So, the main reason for doing both methods was to reduce the interferences of the sample matrix, but later, it allowed to compare the dissolved chromium in solution (no digestion) with the total chromium (digestion).

For dissolved Cr determination (no digestion), samples were filtered with syringe filter units of 0.22 µm and acidified until analysis. For total Cr determination (digestion), 50 mL of sample were digested with 5 mL of nitric acid in a block digester KDIGB6M at 95 ºC for 4 h, according to APHA 3030E. The digestate was filtered with syringe filter units of 0.22 µm, and the filtrate was diluted in a 50-mL volumetric flask. The determination was executed in an ICP-MS Agilent 7800 located in the Chemical Engineering department at IIT Kanpur.

Samples of thickened sludge (SL-TH), mechanically dewatered sludge (SL-MDW), and sludge from lagoons (SL-LG) were dried in an oven at 105 ºC for 48 h prior to digestion. Sludge samples were analysed in Vimta Labs, located in Hyderabad, India, according to the methods EPA 3050B and APHA 3500CrB (U.S. EPA 1996; Baird and Bridgewater 2017).

Cr mass balances

For the Cr mass balance in the STP, data about process flow rate and sludge quantities were obtained from KII. Thus, the measured concentrations of total Cr and Cr (VI) were multiplied by the process stream in each treatment step to obtain the mass flow rate.

For sludge, the measured concentration of total Cr and Cr (VI) has to be multiplied by the sludge's mass to determine the total Cr and Cr (VI) deposited in the sludge. For this purpose, the density of sludge was determined according to mass and volume measurement for SL-TH and SL-LG as described in Velkushanova et al. (2021); density for SL-MDW was measured according to the volume displacement method BS 812-2 (1995) as adapted in Velkushanova (et al. 2021).

3.5.3. Risk assessment approach

The risk assessment was contemplated as the third module of the SSP process described in section 2.4.1. For the case study in the STP in Kanpur, (Babalola et al. 2023) addressed the second and third module of SSP. The present study used the map of the sanitation system made by (Babalola et al. 2023), described in Section 3.3 as a starting point and it was expanded and adapted with the sludge management process. For the risk assessment, the list of hazardous events and hazards displayed in Table 11 and Table 12 were considered and adapted, but only were use those related with the exposure pathways related to chromium to achieve objectives 3 and 4 (Babalola et al. 2023).

Table 11. Hazard identification in STP Jajmau, Kanpur. Source: (Babalola, 2023)

Category	Hazardous event	Hazard
A	Exposure to hazardous gases when working in confined places	Aerosols
		Hydrogen sulfide and malodor
B	Accidents from contact with sharp objects, electrical divices (naked wire) and spillages during daily inspection and sample collection	Falls, slips
		Cuts
		Electric shock
	Falling into the open clarifier	Drowning
C	Exposure to untreated sewage during operation and maintenance of the ST	Microbial pathogens, skin irritants
	Mosquito breeding in surface water	Vector-related diseases
	Musculoskeletal disorder from taking uncomfortable postures during inspection and installation	Musculoskeletal disorder
D	Exposure to high noise level from electromechanical infrastructure	Noise

Table 12. Hazard identification for the farmers reusing the effluent in Kanpur. Source: (Babalola, 2023)

Category	Hazardous event	Hazard	Exposure group (F=farmers, C=children)
A	Exposure to hazardous gases	Malodor	F and C
B	Accidents from falls and slips on a wet and slippery surface while working on the field	Falls, slips	F and C
C1	Exposure during flood irrigation	Microbial pathogens	F
C2		Soil helminths	F
C3		Skin irritants	F
C1	Exposure during farming activities	Microbial pathogens	F
C2		Soil helminths	F
C3		Skin irritants	F
C1	Exposure through playing and helping parents on field	Microbial pathogens	C
C2		Soil helminths	C
C3		Skin irritants	C
C4	Mosquito breeding in irrigation water	Vector-related diseases	F and C
C5	Musculoskeletal disorder from taking uncomfortable postures during farming activities	Musculoskeletal disorder	F
			C

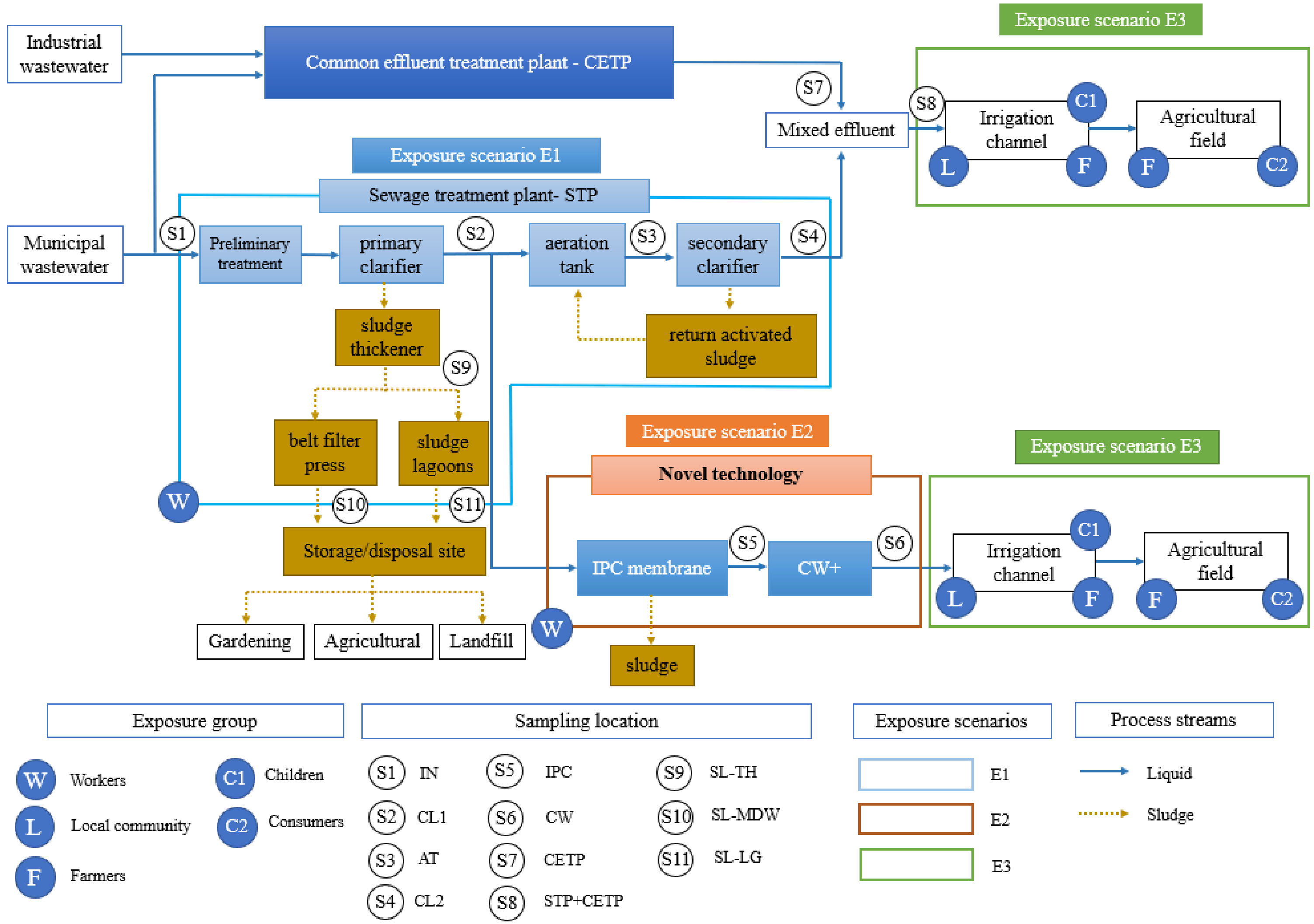
Chapter 4. Results and Discussion

This chapter present the findings based on the KIIs, observations and chromium concentration determinations. It also shows the fate of chromium in the wastewater treatment plant and the health risks assessment related to chemical exposure to chromium.

4.1. Process map for the current STP and novel technology

The system boundary for this study comprises Jajmau STP, the novel technologies IPC and CW+ and the reuse context of reclaimed water for irrigation in the villages of Alaulapur and Kulgaon. The exposure groups of the system boundary are the workers of the STP, the farmers and the children living in the villages. The exposure scenario for workers includes the conventional treatment (E1) and the novel technologies (E2). The irrigation channel and wastewater reuse in agricultural fields comprise the exposure scenario E3. The system's map is shown in Figure 11, along with the identified exposure groups, the sampling points, and the exposure scenarios that define the system boundary. The exposure groups for the irrigation channel are the farmers, the local community and the children. Finally, the exposure groups for the wastewater reuse are the farmers, the consumers and the children playing along the irrigation channels. The proposed sanitation system boundary and exposure groups were based on the previous study by Babalola (2023), with the difference that the boundaries were expanded to include sludge management. It is important to note that exposure groups such as local communities and consumers were identified in the process map; the present study only includes the STP workers, farmers and children in the risk assessment because the focus of the research is occupational health risks due to their high levels of exposure to raw wastewater and partially treated effluent.

Figure 11. Process flow for wastewater safety planning in STP Jajmau, Kanpur



The municipal wastewater is discharged at the STP and in the CETP, but the main characteristic of the CETP is that it receives industrial wastewater from the tanning cluster in Kanpur. The STP was designed to process 130 MLD of municipal wastewater; meanwhile, the CETP was designed to receive 36 MLD of wastewater: 26 MLD of domestic wastewater and 9 MLD of tannery wastewater. However, the CETP is receiving up to 30 MLD of tannery wastewater (K-01), and illegal discharges of tanneries are ending up in the STP. The present study is focused on the STP with a design capacity of 130 MLD, but usually, the flow varies between 90 and 120 MLD (K-01).

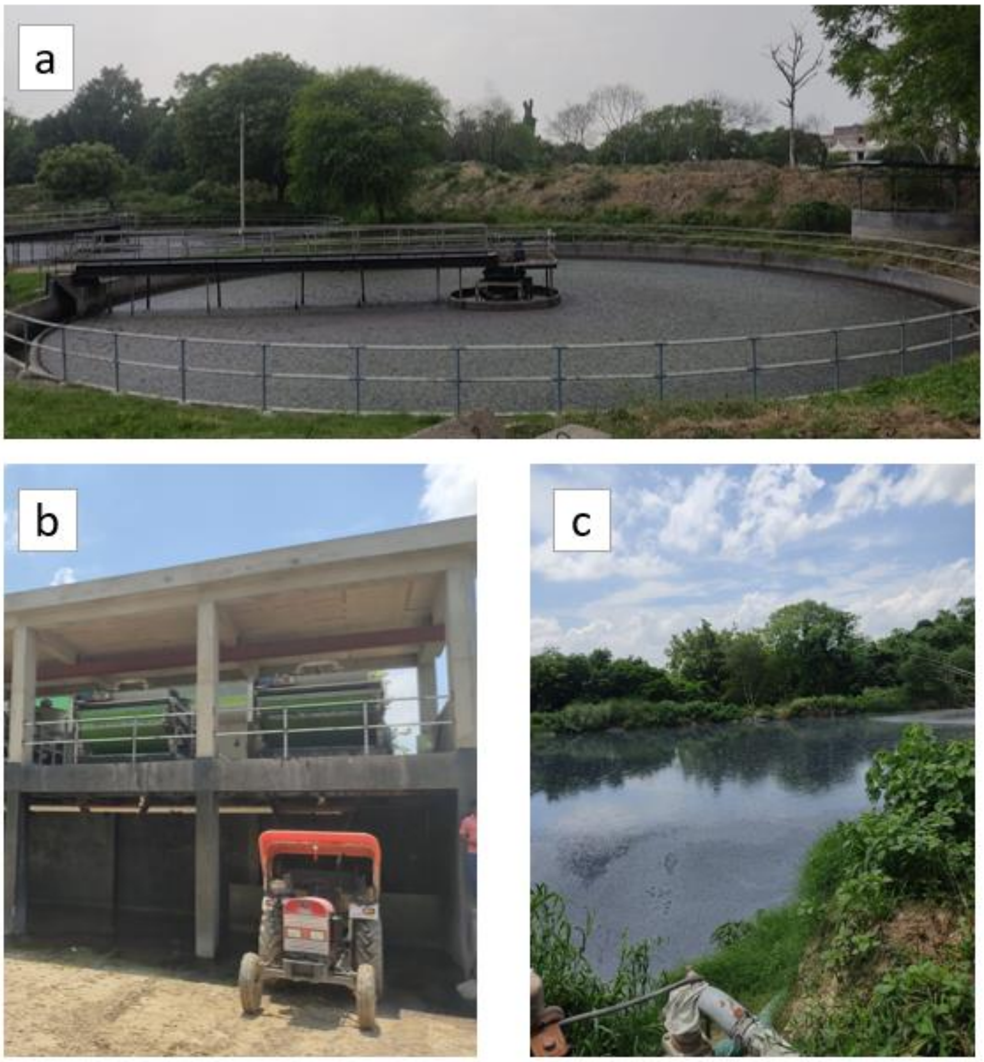
The 130 MLD STP treatment starts with a screen chamber and grit removal as preliminary treatment to remove the coarse debris and floating materials (Figure 12A) (Babalola, 2022). The influent is divided into three parallel streams of primary clarifiers (Figure 12B) as primary treatment, each with a capacity of 43 MLD (K-01). In this step, there is a solid-liquid separation where the particulate matter settles down and is removed from the water stream (Section 2.1). The secondary treatment used is ASP (Figure 12C), and finally, there are three secondary clarifiers for the waterline (Section 2.1).

The effluent of the STP is then mixed with the CETP effluent (Figure 12D), which treats industrial wastewater from the tanneries cluster in Kanpur and municipal wastewater (K-01). The mixing proportion of both effluents is around 65% STP and 35 % CETP (K-02). The mixed effluent is reused in the peri-urban areas for flood irrigation of millet, rice and wheat (Breitenmoser et al. 2022; Babalola et al. 2023), which involves direct contact during farming activities, as will be discussed in Section 4.6. The novel technology implemented in the innovation site by the Pavitra Ganga project comprises an IPC membrane system (Figure 12E) and constructed wetlands (Figure 12F) (Babalola, 2022).

Figure 12. 130 MLD STP treatment train and novel technologies

For sludge management, the STP uses gravity thickeners, mechanical dewatering and nature-based solutions as drying beds and sludge lagoons, as shown in Figure 13 (K-01). The liquid from the thickener and dewatering system is returned to the water stream (Figure 11) (K-01). Under normal conditions, the primary sludge is thickened and mixed with the secondary sludge. According to K-01, 75-80% of the activated sludge is recycled and returned through the return sludge pump house in normal operations, and 25-30% is discarded. However, during the study, all the sludge was returned to the system, so the only sludge produced was primary sludge (Figure 11). Two belt filter presses operate continuously with maximum performance in the monsoon when the drying beds performance is poor. There are 38 drying beds in the STP with an approximate area of 400 m^2 each. However, during the structured observation, there were identified sludge lagoons in use during operation instead of drying beds (Figure 13).

Figure 13. a) sludge thickener; b) Mechanical dewatering site; c) sludge lagoon



The sludge is then collected by trucks every three or four months (K-02) and transported to a designated place far away from the STP but inside the facility's premises comprising the STP and the CETP systems (K-02). This storage/disposal site is not managed by the STP or CETP but by the Kanpur Nagar Nigam (Kanpur Municipal Corporation, KMC), where it is reused for fertilizer, principally for gardening activities (K-01). The sludge is also reused by other farmers who do not use the mixed STP-CETP effluent for irrigation. "*If they need sludge, they come to the dumping site to collect it, but it is managed by the KMC*", said K-01. In contrast to earlier research made by Babalola et al. (2023), this process flow for wastewater sanitation planning in Jajmau STP Kanpur and villages reusing the effluent expands the information regarding sludge management and sludge fate and assesses the novel technologies already being piloted in the innovation site.

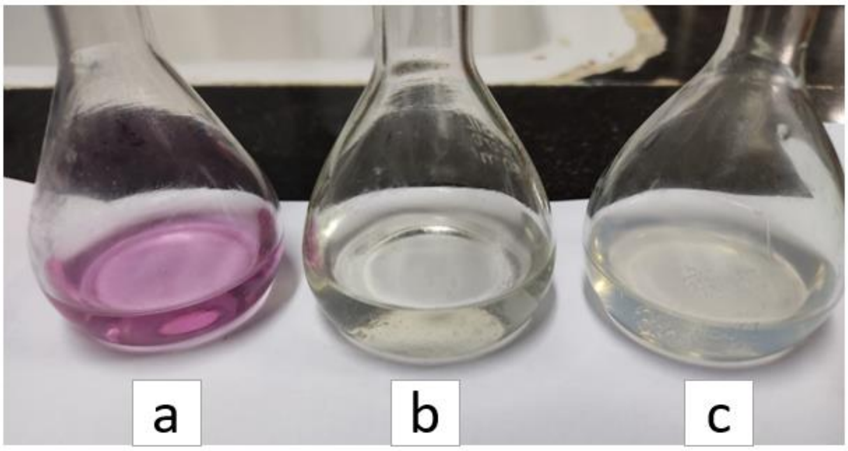
4.2. Concentrations of total Cr and Cr (VI)

Table 13 shows the concentrations of total chromium and hexavalent chromium in the different process streams of the treatment train mentioned in section 3.5.2 and explained in Figure 11 during the three campaigns. It is important to highlight that total chromium represents the presence of the two chromium species: trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)], as discussed in section 2.4.5.

Regarding Cr (VI), since the first campaign, all of the taken wastewater samples were below the limit of detection (Table 13), which is 100 μg/L for the colourimetric method for hexavalent chromium determination with diphenylcarbazide (3500-Cr B) (Baird and Bridgewater 2017). The diphenylcarbazide method is based on the oxidizing properties of Cr (VI) that react at low pH with 1,5-diphenylcarbazide to give a violet solution (Marczenko and Balcerzak 2000). The coloured product of this reaction is measured in UV-Vis at λ= 540 nm (Marczenko and Balcerzak 2000). Hence, the colour intensity of the reaction is proportional to the concentration of Cr (VI) in the sample. Figure 14 shows that samples do not display any colouration change.

These results are aligned with the information about the predominant presence of trivalent chromium in tannery wastewater as the main reagent used for tanning is chromium (III) sulfate (BCS), and indicates that there is no conversion taking place between Cr(III) and Cr(VI) which is a positive outcome considering the carcinogenic effects of hexavalent chromium discussed in Section 2.4.6 and the concerns regarding hexavalent chromium in wastewater. This also indicates that total chromium concentrations in Table 13 are mainly constituted by trivalent chromium.

Figure 14. Change of coloration: a) standard 0.5 mg/L Cr; b) influent STP; c) effluent CETP



Total chromium concentrations were determined for non-digested and digested samples according to the procedure described in section 3.5.2. Digested samples have higher chromium concentrations than non-digested ones in all cases (Table 13). This is because acid digestion releases the forms of metal associated with particulate matter, whereas the no-digested samples only account for the dissolved chromium, showing that a significant portion of the chromium is associated with the particulate matter. For example, after the aeration tank (AT), digested samples are 3.8 times more than non-digested samples in total chromium concentrations (Table 13). Changes in digested vs. non-digested concentrations are notably different in samples that contained more organic matter as AT and STP+CETP, where digested samples are up to 24 times non-digested concentration. These results are consistent with the occurrence of trivalent chromium mentioned in the literature and its tendency to form insoluble complexes or to be absorbed by particulate matter (Gomez and Callao 2006; Ahemad 2014).

One key observation is that digested samples results show the concentration of both the dissolved chromium and the associated chromium to organic matter, hence, they provide information about the overall metal load in the wastewater samples. For this reason, the digested concentrations would be used onwards to compare the total Cr loads into the STP, the mass balance in Section 4.3, and the health risk assessment, and they will be called total Cr from this point.

Table 13. Total Cr concentrations of different process streams STP Jajmau

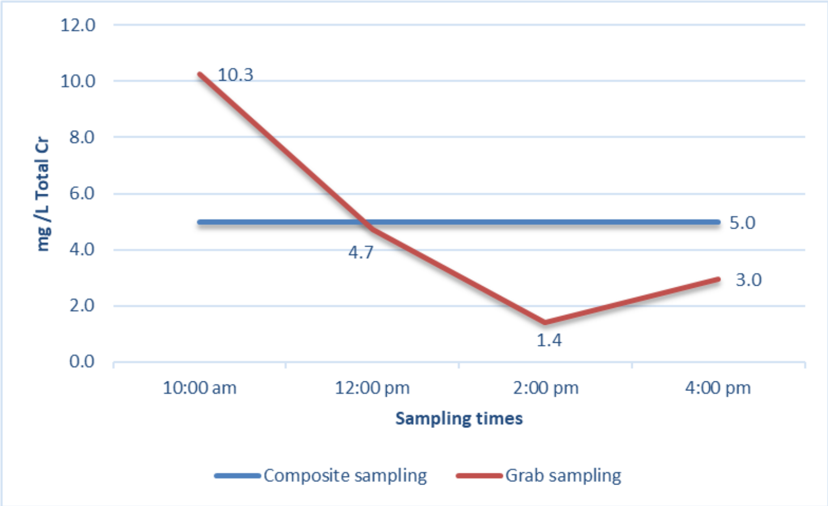
Sampling point	Sample	First campaign				Second campaign				Third campaign			
		Total Cr (mg/L)			Cr(VI)	Total Cr (mg/L)			Cr(VI)	Total Cr (mg/L)			Cr(VI)
		No digestion	Digestion	S.D.		No digestion	Digestion	S.D.		No digestion	Digestion	S.D.	
S1	IN	11.0	14.2	0.7	below 100 µg/L	1.0	2.6	0.1	below 100 µg/L	4.0	5.0	0.2	below 100 µg/L
S2	CL1	1.1	1.9	0.2		0.05	0.77	0.09		1.05	1.50	0.01	
S3	AT	15.0	44.6	1.1		12	44	13		13	19	3	
S4	CL2	0.09	0.21	0.01		0.0496	0.1331	0.0007		0.106	0.235	0.002	
S5	IPC	0.030	0.046	0.003		0.019	0.033	0.003		0.018409	0.028656	9.5E-06	
S6	CW	0.030	0.041	0.001		0.014	0.026	0.001		0.0175	0.0272	0.0005	
S7	CETP	2.324	2.980	0.001		2.5	3.3	0.3		2.7	3.3	0.2	
S8	STP+CETP	0.06	1.46	0.1		0.56	0.87	0.08		0.28	2.09	2.1	
S9	SL-TH (mg/kg)	-	14,913*	2265	0.24*	-	19,136*	2265	0.07*	-	15,604*	2265	0.39*
S10	SL-MDW (mg/kg)	-	8,672*	4463	0.67*	-	17,525*	4463	0.49*	-	14,088*	4463	0.04*
S11	SL-LG (mg/kg)	-	15,045*	799	0.28*	-	16,296*	799	0.52*	-	16,532*	799	0.63*

Note: *units mg/kg.
The number of significant figures is related to the standard deviation of the measurements.

The influent concentrations are highly variable, going from a minimum of 2.6 mg/L up to 11.0 mg/L of total Cr (Table 13), between 64 and 275 times more than the typical for municipal wastewater comprising mainly domestic wastewater and minor contributions of industrial wastewater, where chromium concentrations are between 0.01 mg/L and 0.04 mg/L (Henze et al. 2002). These findings support the hypothesis of illegal discharges of tannery wastewater in the sewage that should be discharged to the CETP. However, there is no pattern in the influent concentrations during the campaign days, and the variability of the concentrations can be related to the fact that the sampling was undertaken during monsoon season, especially since the second campaign was executed after heavy rain the day before, so heavy rains might dilute the heavy metals content. Similarly, chromium variability can be related to different activities and working patterns in the upstream tanneries. In consequence, there would be expected higher values during the dry season.

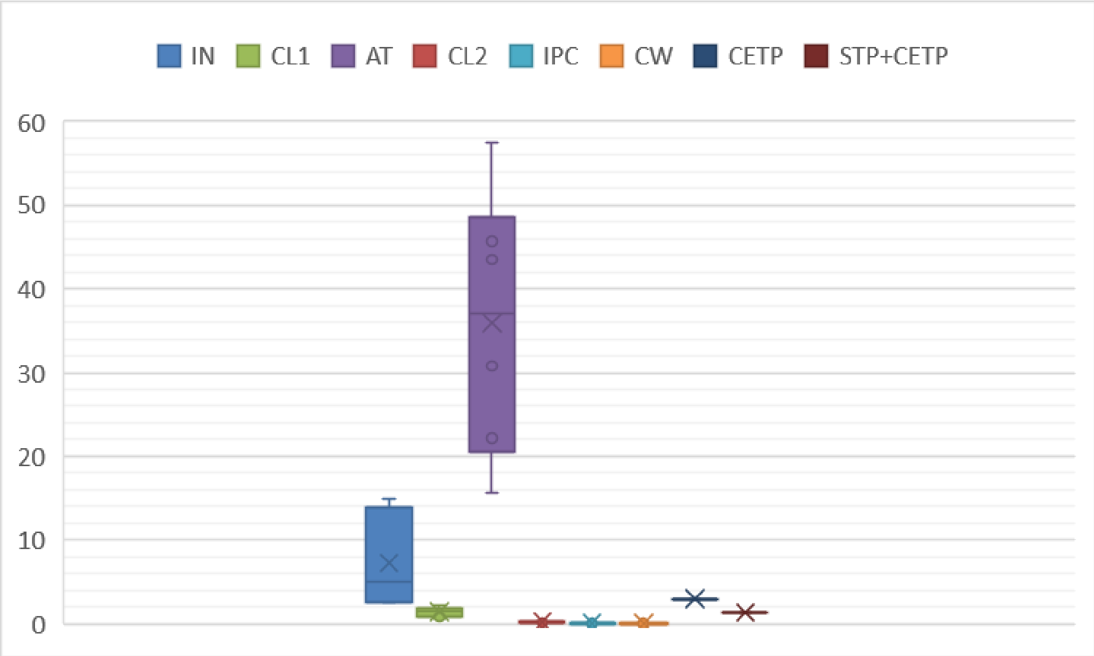
During the third campaign, grab samples of the influent were taken at intervals of two hours (Figure 15) to explore if there was a change in the chromium concentrations along the day, as mentioned in Section 3.5.2. Figure 15 compares grab samples of the influent and composite sampling (Table 13). The data reveals that the concentration of Cr in the influent varies along the day, with the highest peak in the morning and a decrease along the day, with a subtle increment in the afternoon (Figure 15). K-02 stated that in normal operation conditions, the volume of wastewater is higher during the morning between 6 am and 12 pm and lower in the afternoon. The average concentration of grab sampling is 4.8 mg/L, and the obtained concentration from the composite sampling is 5.0 mg/L, which demonstrates that composite sampling accounts for the average chromium concentration and it is a suitable method to analyse the chromium loads in the STP, as discussed in section 3.5.2

Figure 15. Variation of influent Cr concentrations



There is a significant reduction of around 90% of the concentration after the primary clarifier, which can suggest the migration of total Cr to the primary sludge (Figure 16), as expected, considering that the predominant species is trivalent chromium and it tends to associate to particulate matter (Section 2.4.5). However, the Cr concentration after the aeration tank increases notably, as shown in Figure 16. This suggests the accumulation of chromium in the aeration tank due to adsorption by the activated sludge, as reported by (Vaiopoulou and Gikas 2012). It is also supported by the relation between the concentration of dissolved chromium (non-digested) and chromium bound to organic matter (digested), as shown in Table 13. The high presence of chromium in the STP can affect the efficiency of the ASP treatment by altering COD removal efficiency due to the competition between organic matter and heavy metals for binding to the surface of the biomass, which is currently being completely recirculated into the system as observed during the sampling campaigns. In addition, this build-up of chromium in the biomass can pose a risk to the STP workers, as discussed in Section 4.4, due to high concentrations.

Figure 16. Total Cr concentrations in different process streams



Chromium concentrations after the secondary clarifier (CL2), the effluent of the STP conventional treatment, are around 0.13 to 0.23 mg/L (Table 13), which represents a reduction of 97% of the total Cr concentration in the influent, but it is still up to two times above the maximum permissible concentration of toxic elements according Indian standard for irrigation water (0.1 mg/L) (CPHEEO, 2013).

Regarding the novel technologies, total Cr concentrations after the IPC membrane and CW+ are between 0.02 and 0.04 mg/L (Table 13), complying with the permissible standard (0.1 mg/L). Considering that the novel technology takes the effluent from CL1, as shown in Figure 11, the total Cr reduction is 97.7% compared to CL1 concentrations, higher than the reduction of 86% reduction in chromium levels due to the activated sludge process (Table 13).

Cr concentrations in CETP effluent are around 2.98 and 3.27 mg/L (Table 13) meanwhile, after the mixing of the STP and CETP effluent in a ratio of 65-70% of STP effluent and 30-35% of CETP (K-02), the final concentrations of Cr in the irrigation channel are between 0.87 and 2.09 mg/L, from 8 to 20 times higher than the maximum permissible limit (0.1 mg/L).

For sludge samples, Table 13 shows the total and hexavalent chromium concentration found in the three sampling points mentioned in Section 3.5.2. Hexavalent Cr concentration is notably lower than total Cr in sludge samples, as determined in wastewater samples (Table 13).

Although Cr(VI) is more soluble than Cr(III), the anions are easily reduced to Cr(III) by organic matter as electron donors, leading to lower concentrations of Cr(VI) (Dhal et al. 2013).

Higher values of Cr(VI) were found in the sludge from the lagoons and the mechanically dewatered sludge. Total Cr values are extremely high, with a range between 13,428 to 15,957 mg of total Cr/kg of sludge, compared with concentrations of tannery sludge (8,041 mg/kg), showing that chromium is being accumulated in the sludge (Kiliç et al. 2011). The sludge deposited in the lagoons contains a higher concentration of total Cr. These concentrations of total Cr in sludge are up to 5 times higher than the maximum concentration limit for biosolids application to land (3,000 mg/kg) (Walker 1994). It was expected to find mainly trivalent chromium species, but it was surprising to obtain extremely high values of sludge, considering that it is coming from the CETP and not from the STP. Earlier studies had found total chromium concentrations in sludge in Kanpur between 25,030 to 27,557 mg/kg (Kumar et al. 2023) and up to 50,000 mg/kg (Apte et al. 2005), but in chromium-contaminated tannery sludge dumping ground.

Although trivalent chromium is much less toxic than hexavalent chromium, changes in the speciation of the cation due to environmental conditions can affect bioavailability and toxicity (Gomez and Callao 2006). For instance, although chromium is predominantly present as Cr(III) in the soil, under oxidizing agents such as manganese and lead oxides and high pH, Cr(III) can be oxidized to Cr(VI), which is a serious environmental concern. For instance, earlier research has found hexavalent chromium in sludge and soil samples from a tannery sludge dumping in Kanpur, even though fresh sludge contained little hexavalent chromium (Apte et al. 2005). However, these circumstances are mediated by the pH, redox potential, and availability of water-soluble species present as mobile Cr (III) (Dhal et al. 2013).

4.3. Mass balance

Daily mass flow rates of Cr in the STP process streams (K-01) are tabulated in Table 14 and displayed schematically in Figure 17. Even though values of total Cr were highly variable in sampling points such as influent and aeration tank, the mass balance was made under the assumption of an average value of the whole campaign period. For mass concentration of total Cr in sludge, density and total solids TS were determined (Table 15).

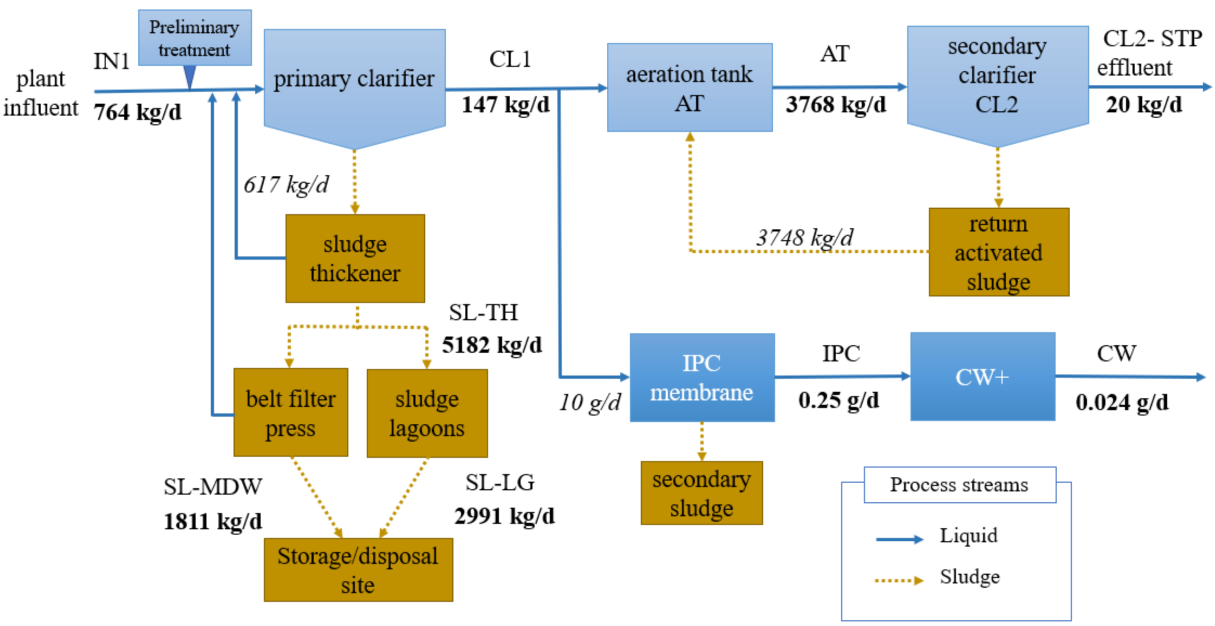
Table 14. Characteristics of sampled process streams

Process stream	Flow rate	Total Cr (mg/L)	Cr mass flow rate (kg/day)
Plant influent	105 MLD	7.27	764
Primary clarifier	105 MLD	1.40	147
Aeration tank	105 MLD	35.88	3768
Secondary clarifier	105 MLD	0.19	20
Thickened sludge	352 m3/d	14722	5182
Dewatered sludge	143 m3/d	12662	1811
Sludge from lagoons	191 m3/d	15660	2991
IPC	7000 L/d	0.04	2.5*10-4
CW+	750 L/d	0.03	2.4*10-5

Table 15. Density and Total Solids of sludge samples

Sample	*Density*	*T.S.*
SL-MDW	0,94	0,28
SL-TH	0,89	0,14
SL-LG	0,98	0,12

Figure 17. Schematic diagram showing Cr variation in the process streams Measured values are shown in bold and calculated values are shown in italics



The mean daily mass rate of Cr entering the plant in the influent stream was 764 kg/day. Primary treatment account for the removal of 617 kg/day (Figure 17), which represent an 80% reduction

(100*(764-147)/764) of the chromium mass from the water stream; this amount of chromium stays in the sludge. The exiting daily load of total Cr in the plant was 20 kg/day (Table 16, Figure 17), which suggests that the overall liquid removal of Cr at the plant is 97% (100*(764-20)/764).

617 kg total Cr/day stays in the primary sludge, and chromium concentration increases 8.3 times after the thickening (5,812 kg/d, as shown in Figure 17). This can be due to the concentration of the sludge during thickening and dewatering while the liquid fraction is removed and returned to the water streams (Metcalf & Eddy Inc., 2003). After thickening, chromium concentration is split during the following processes, where 40% is dewatered mechanically, and the remaining is discharged in sludge lagoons (K-01). Consequently, the high concentration of total Cr in the sludge line suggests heavy metal accumulation in the sludge, with daily loads of around 1810 and 2991 kg of total Cr that are removed every 3 to 4 months to the disposal site. Prior to the present study, it was not expected to find such high concentrations of total chromium in the sludge. However, considering the chromium variation in the process (Figure 17), 80% (100*(764-147)/764) is remaining in the sludge and being separated from the process during primary treatment and ending up in the storage/disposal site (Figure 11) since there is no further treatment.

The closure of the chromium mass balance, excluding the sludge management beyond thickeners, is 83% (100*(617+20+2.4*10-5)/764), which implies that 127 kg enters the plant daily and does not leave. The explanation for this can be related to the chromium accumulation in the ASP (Figure 17) and the complete recirculation of the activated sludge, as discussed earlier in section 4.2.

Regarding the novel technologies, due to the volume of the pilot, the influent of the IPC membrane contains 10 g total Cr/d (Figure 17). In comparison, the effluent only contains 0.25 g total Cr/d. This shows a reduction of 97% chromium in the water stream (100*(10-0.25)/10). The chromium reduction done by the CW+ is 90% (100*(0.25-0.024)/0.25).

It is important to note that even though the CW+ is reducing chromium in 90% of the daily mass, that calculation is influenced by the low volume of the system (Table 14). Most of the removal is done in the previous step (IPC membrane), and the mean concentration of total Cr is already below the maximum permissible limit (0.1 mg/L) after the IPC membrane, as shown in Table 15. So, these results have significant implications for further steps in the innovation site. If there is an interest in the removal of chromium in Jajmau STP, the technical focus should be on the sludge treatment rather than the effluent, as 4/5 of chromium is being accumulated in the sludge and considering chromium, CW+ is working as a polishing step.

4.4. Health risks assessment attributed to current STP

The hazardous events identified previously by Babalola (2023) and discussed in Sections 2.4.4 and 3.5.3 were used as the basis for this study, considering only those directly related to chromium exposure. In addition, the ILO checklist was also considered, as well as structured observation and information coming from interviews of key informants. The likelihood was assessed according to the semiquantitative risk assessment explained in section 2.3.2. The severity of chromium exposure was assessed according to the total concentration of chromium in the different treatment steps discussed in section 4.2 (Table 13).

The main occupational chromium exposure pathways are through dermal contact, accidental ingestion and inhalation (aerosols), which can result in diseases from exposure to wastewater and sludge containing chromium (Sun and Costa 2022). Even though hexavalent concentrations are below 100 μg/L, which is a positive outcome considering its toxicity and carcinogenic effects (Section 2.4.6), trivalent chromium levels are extremely high in the influent of the STP and along the treatment train as well as in the sludge (Table 13/ Section 4.2).

In this regard, hazardous events are related to exposure to untreated and partially treated sewage during operation and maintenance, and it is present throughout the whole treatment train: preliminary treatment, primary and secondary treatment. The preliminary treatment included operation activities such as collecting the debris in the screen chamber and cleaning the machines involving the exposure to chromium-containing materials coming from the tanneries, such as flesh and hair – one of the significant characteristic waste of the leather industry (Puhazhselvan et al. 2022) – that were observed to be collected in the screen chamber (Figure 18). For secondary treatment, aerosols containing untreated sewage are hazardous for workers.

Figure 18. Screen chamber debris containing fleshes and hair in preliminary treatment at STP Jajmau

Regarding the sludge management, treatment steps such as sludge thickening, sludge mechanical dewatering and sludge disposal involve direct contact of workers with sludge. According to K-02, there is normally one worker in each site (thickening and dewatering) during a working period of hours. His main work is to give instruction for machines operations, so they don't have contact with the sludge (K-02). However, there are sweepers who deal directly with sludge, in tasks of removing the debris from tanks or remove materials from pipes. They are in direct contact with sludge minimum 30 minutes every day (K-02). According observation, during sludge thickening, hazardous event can occur while removing debris from the borders of the thickener. In addition, it was observed in the mechanical dewatering site, the cleaning activities of the belt filter press involves a direct contact with sludge.

The exposure groups identified in the mapping process are the STP workers (W1), which comprises the exposure scenario E1. The main exposure occupational pathways related to chromium in this scenario are at first skin contact and in less degree inhalation, especially when the workers are in contact with aerosols (Table 16), because chromium is mainly present in dissolved and associated form and not in mist (Section 2.5.6). In addition, accidental ingestion was also considered specially during cleaning processes in preliminary treatment, primary treatment and sludge handling where there is spillage and safety measures as handwashing and mask are not met in place, as observed during the sampling campaign.

According K-02, there are no long-term skin problems, but workers who deal directly with sludge "*experience a burning sensation in the skin that remains for some time"*. On the contrary, Babalola (2022) reported skin irritation as a similar issue in the STP.

The existing control measures within the STP includes the use of PPE: gloves, safety boots, helmets, safety belts. Although workers are instructed to use PPE, these elements are not always provided (Babalola, 2022). During the structured observation, workers were observed without any PPE doing the operation activities without the use of gloves or safety boots leaving hands and legs exposed to untreated sewage.

For Cr exposure, the likelihood of the hazard identification was assessed as possible (L= 3) following the classification mentioned in Section 2.4.2 (Table 4), described as a hazardous that "it may have happened in the past and may occur under regular circumstances in the next 12 months or another reasonable period". Of particular significance is that WHO identifies heavy metals associated with wastewater use in agriculture (Section 2.4 /Table 3) as low importance but this study shows that chromium concentrations are up to 275 times more than typical municipal concentrations discharging in an STP, which implies occupational risks for workers and farmers (as will be discussed in section 4.6). These results have significant implications in how heavy metals pose a long-term risk in wastewater use in agriculture, in particular in health risk mitigation focus for moving from unplanned use to planned used of wastewater irrigation types, at least in terms of water quality and water reuse guidelines (Table 1/Section 2.3).

In consequence, the severity was assessed regarding the Cr concentrations in each step of the treatment train mentioned above (Table 13), contrasting them with the maximum concentration of chromium in irrigation water (0.1 mg/L). The treatment steps with highest Cr concentration were classified as major severity, resulting in illness or injury, meanwhile the treatment steps with Cr below the threshold (0.1 mg/L) were classified as insignificant risk. For concentrations above the threshold and up to 10 times the maximum limit, the severity was considered as minor health effects and finally, more than 10 times it was assumed to have a moderate risk in the long term. The outcome of the risk assessment conducted for the STP is shown inTable 16.

Table 16. STP processes risk assessment

Treatment process	Hazard Identification				Existing control measure	Risk Assesments L=Likelihood, S=Severity, R=Risk level			
	Hazardous event	Hazard	Exposure route	Exposure group	Description	L	S	score	R
Preliminary treatment	Exposure to untreated sewage during operation and maintenance of the ST	Skin irritants	skin contact, accidental ingestion		Use of PPE:gloves, boots, face mask, regular handwashing	3	2	6	M
Primary treatment (primary clarifier)	Exposure to untreated sewage during operation and maintenance of the ST	Aerosols	Inhalation		Use of PPE:face mask	3	2	6	M
	Exposure to untreated sewage during operation and maintenance of the ST	Skin irritants	skin contact, accidental ingestion		Use of PPE:gloves, boots, face mask, regular handwashing	3	2	6	M
Secondary treatment Activated sludge process and secondary clarifier	Exposure to untreated sewage during operation and maintenance of the ST	Aerosols	Inhalation	Exposure scenario (E1) Workers	Use of PPE:face mask	3	4	12	M
	Exposure to untreated sewage during operation and maintenance of the ST	Skin irritants	skin contact,		Use of PPE:gloves, boots, face mask, regular handwashing	3	4	12	M
Sludge thickening	Exposure to untreated sludge during operation and maintenance of the ST	Skin irritants	skin contact accidental ingestion		Use of PPE:gloves, boots, face mask, regular handwashing	3	8	24	H
Sludge mechanical drying	Exposure to untreated sludge during operation and maintenance of the ST	Skin irritants	skin contact		Use of PPE:gloves, boots, face mask, regular handwashing	3	8	24	H
Sludge lagoons	Exposure to untreated sludge during operation and maintenance of the ST	Skin irritants	skin contact		Use of PPE:gloves, boots, face mask, regular handwashing	3	8	24	H

4.5. Health risks assessment for the novel technology

The boundaries of the exposure scenario E2 comprises the pilot novel technologies located in the innovation site of the STP Jajmau and comprises the workers operating the new technology (W2). The IPC membrane receives the effluent from the primary clarifier, and it treats around

7000 L/d (K-03). The permeate flows to the constructed wetland plus (CW+) that treats around 750 L/d (K-04). The possible risks associated with this technology are similar to the activated sludge process used in the conventional treatment (Babalola et al. 2023). Regarding the sludge handling, as mention in section 3.3, the IPC technology produces less sludge than conventional ASP, which reduces the sludge handling frequency for the workers. In addition, during the present study, the pilot had not produced enough sludge to do maintenance.

As mentioned in section 2.5.6, the occupational exposure pathways related to Cr exposure includes inhalation, accidental ingestion and direct dermal contact (Sun and Costa 2022). However, due to process changes in the technology compared to the conventional treatment ASP, the exposure is less, so the exposure routes of accidental ingestion and inhalation (aerosols) were not contemplated.

Although the likelihood of the hazardous events remains similar to the conventional treatment process, the severity is much less due to the low concentration of Cr during the treatment steps of the novel technologies. Meanwhile the reduction of 90% of the Cr concentrations is made in the primary clarifier, the influent arriving to the novel technologies has an average concentration of 1.4 mg/L and the effluent of the IPC is around 0.04 mg/L, which is 35 times less that the influent concentration. The Cr concentration are below the maximum limit of the guideline, so the severity was classified as insignificant (S=1), that means that the hazardous events results in no or negligible health effects compared to the background levels. Table 17 displays the risk assessment conducted for the STP in the exposure scenario E2.

It is important to note that the novel technologies only modify the secondary treatment of the treatment train, so the preliminary and primary treatment risk assessment remains the same as in section 4.4, even if they are not included in Table 17.

Table 17. Novel technologies processes risk assessment

Treatment process	Hazard Identification				Existing control measure	Risk Assesments L=Likelihood, S=Severity, R=Risk level			
	Hazardous event	Hazard	Exposure route	Exposure group	Description	L	S	score	R
Secondary treatment- IPC membrane	Exposure to untreated sewage during operation and maintenance of the ST	Skin irritants	skin contact	Exposure scenario (E2) Workers	Use of PPE:gloves, boots, face mask, regular handwashing	3	1	3	L
Secondary treatment- Constructed wetland +	Exposure to untreated sewage during operation and maintenance of the ST	Skin irritants	skin contact		Use of PPE:gloves, boots, face mask, regular handwashing	1	1	1	L
Secondary sludge handling	Exposure to untreated sludge during operation and maintenance of the ST	Skin irritants	skin contact		Use of PPE:gloves, boots, face mask, regular handwashing	3	1	3	L

4.6. Health risks assessment for irrigation reuse

The exposure scenario E3 comprises the nearby villages reusing the mixed STP and CETP for irrigation of crops, as explained in section 4.1, in particular Alaulapur and Kulgaon. As the two villages have the same flood irrigation practices and the chromium concentration is the STP+CETP effluent (S8), they were considered for the same risk assessment (Babalola et al. 2023).

From the mapping process (Figure 11) discussed in section 4.1, the exposure groups identified were farmers (F1), local community living in the surroundings of the irrigation channel (L), children (C1) and consumers (C2) of the crops. But, due to the occupational health risk focus of this study, the only exposure groups considered for the risks assessment are farmers (F1) and children (C1). Both F and C1 are only exposed to the mixed effluent STP+CETP (section 4.1) during the farming practices since the sludge is not being reused in the villages (K01-K02). Also, the farmers (F1) and children (C1) are exposed again during the preparation of contaminated crops as they consume the crops grown for their own intake (Babalola et al. 2023) (Babalola 2022).

From the hazardous events identified earlier by Babalola et al. (2023), the main activities where farmers are exposed to Cr in the mixed effluent STP+CETP are during flood irrigation and during farming activities. For children, the exposure can occur when they are playing and helping parent on the field. No hazardous activities were added to the risk assessment regarding sludge reuse since Alaulapur and Kulgaon are only reusing the mixed effluent (K-01).

As discussed by Babalola (2022), 82% (n=11) of the interviewed farmers reported not using PPE, and none of the farmers was observed using PPE in their activities. So, there is no control measure taken to reduce the associated risks of exposure to the irrigation effluent.

The exposure pathway for occupational exposure to chromium are inhalation and dermal contact as discussed in Section 2.5.6. The farmers (F1) are continuously exposed to the STP+CETP effluent during their work activities so the likelihood of the hazard activities is almost certain (5). Regarding the severity, the comparison value was the obtained concentration of total Cr in the STP+CETP mixed effluent. Total Cr concentrations are between 0.87 to 1.46 mg/L, that means between 8 and 14 times higher than the maximum permissible limit for irrigation water (0.1 mg/L) (CPHEEO 2013). However, it is important to consider that the standard is related only to the toxic effects of chromium related to plant growth, hence, it only assesses the agronomic parameters of the irrigation water but not the human-health related parameters to chemical exposure. For Cr (VI), the safe threshold recommended by WHO in wastewater and soils used for agriculture are 0.05 and 0.1 ppm (Kinuthia et al. 2020), and the concentration found in this study for Cr(VI) was below the limit of detection (100 μg/L) as mentioned in section 4.2.

In this sense, considering that Cr(VI) is the most toxic species and concentrations are below the threshold (0.05 mg/L) (Section 4.2), no catastrophic or major severity was considered. However, it is important to note that even though currently the ecotoxicological studies and standards are biased toward Cr(VI), increasing evidence suggest that Cr(III) can cause adverse effects in humans and aquatic organisms and prolonged exposure to high Cr(III) can affect human skin and lungs (Aharchaou et al. 2022b), as previously discussed in section 2.5.6. Therefore, considering that total Cr concentrations were up to 10 times higher than the threshold, severity was considered as moderate since hazard or hazardous event potentially result in self-limiting health effect or minor illness. Table 18 displays the risk assessment conducted for the farmers and children (F and C1) in the exposure scenario E3 (Figure 11/Section 4.1).

Table 18. Wastewater reuse risk assessment

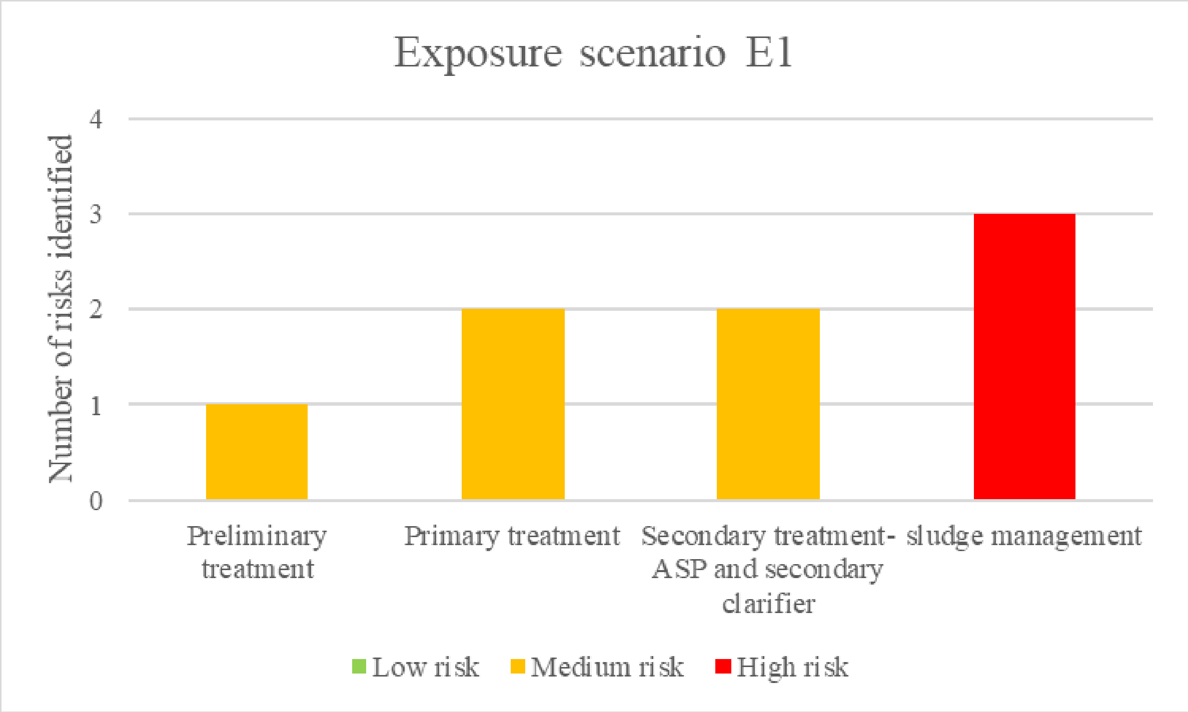
Hazardous event	Hazard	Exposure route	Exposure group (F=farmers, C=children)	Existing control measure	Risk Assesments L=Likelihood, S=Severity, R=Risk level			
					L	S	score	R
Exposure during flood irrigation	Skin irritants	skin contact	F	None	5	4	20	H
Exposure during farming activities	Skin irritants	skin contact	F	None	5	4	20	H
Exposure through playing and helping parents on field	Skin irritants	skin contact	C1	None	5	4	20	H
Exposure during preparation of contaminated crops	Intake of contaminated food with chromium	ingestion	F and C1	Cooked before consumption	5	4	20	H

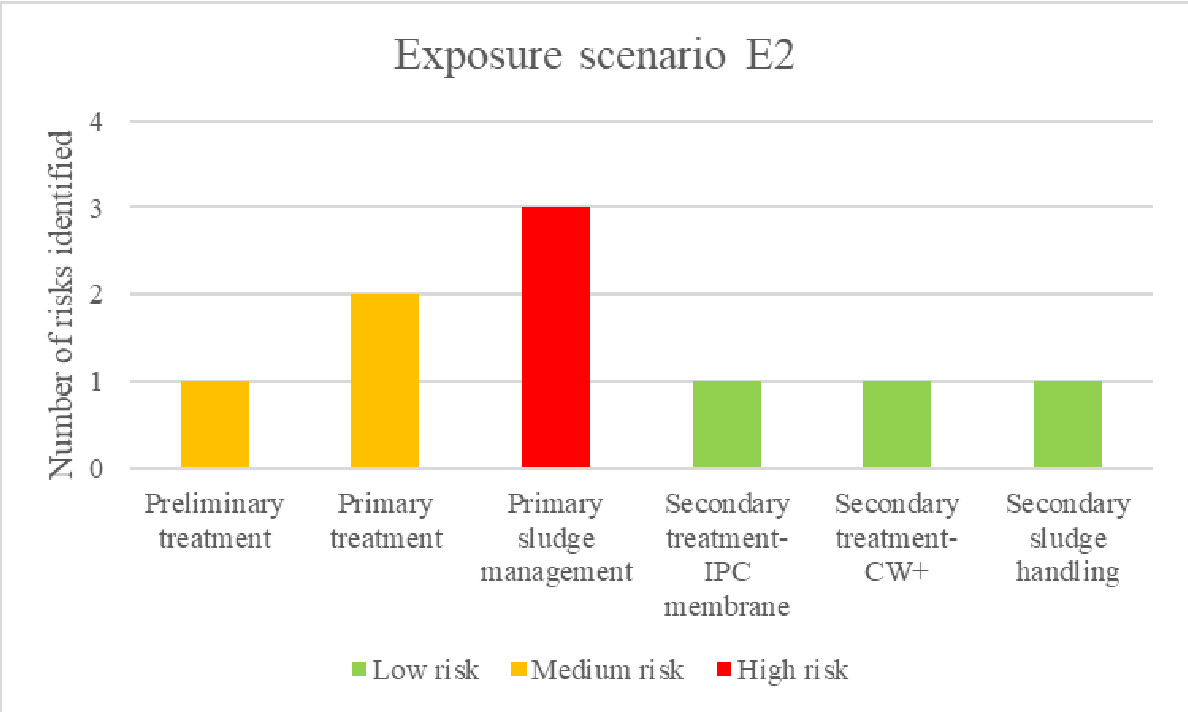
4.7. Comparison of Pavitra ganga novel technology on the occupational health risks for the STP workers

Figure 19 shows the comparison of the health risk levels for STP workers in the two exposure scenarios E1 and E2 (Section 4.1). For the exposure scenario E1, there were identified 8 risks along the treatment train (5 medium, 3 high), meanwhile for the exposure scenario E2 there were identified 9 risks (3 low, 3 medium and 3 high).

As discussed in section 4.5, the novel technologies are applied as secondary treatment, and the risks related to preliminary and primary treatment still remained if the novel technologies were implemented in full scale. In this regard, the data reveals that the risks associated with secondary treatment change from medium to low risk (Figure 19) when novel technologies are implemented. Medium risks were identified for the conventional ASP system due to the exposure to aerosols and skin contact and the high concentration of total chromium in the aeration tank (Figure 16). Low risks were identified for the IPC membrane technology based at first in the less exposure to partially treated sewage due to the enclosure of the system. In second place, even when the chromium levels in the effluent of the IPC are lower than in the ASP, and the chromium is bounded to organic matter in the sludge, the process is designed to produce less sludge and in consequence, there might be less frequent sludge handling (Section 3.3) which again impacts in the exposure to secondary sludge (Figure 19).

Figure 19. Comparison of the health risk levels for STP workers in exposure scenario E1 (above) with exposure scenario E2 (below)





4.8. Comparison of Pavitra ganga novel technology on the occupational health risks for the farmers

The chromium levels in the effluent of the STP and the CETP were presented in section 4.2. The results indicate that treated wastewater from the STP has between 0.13 to 0.23 mg total Cr/L, meanwhile effluent from the CETP has between 2.98 to 3.3 mg total Cr/L. So, Cr concentrations coming from the CETP are up to 22 times higher than in the STP effluent, even though is proportion in the irrigation channel is around 35% (Section 4.1). This indicate that chromium risks exposure is coming mainly from the CETP process, as expected considering that it treats directly industrial effluent coming from the leather tanneries (Section 2.5.1) but showing that it is not complying with the maximum permissible limit (0.1 mg/L), hence, posing a risk for the wastewater reuse scheme. The impact of implementing a novel technology in the STP will not have a great impact in the water for irrigation as the highest concentrations of chromium are coming from the CETP (Table 19).

Table 19. Health risks assessment for the farmers comparing the conventional technology and the novel technology

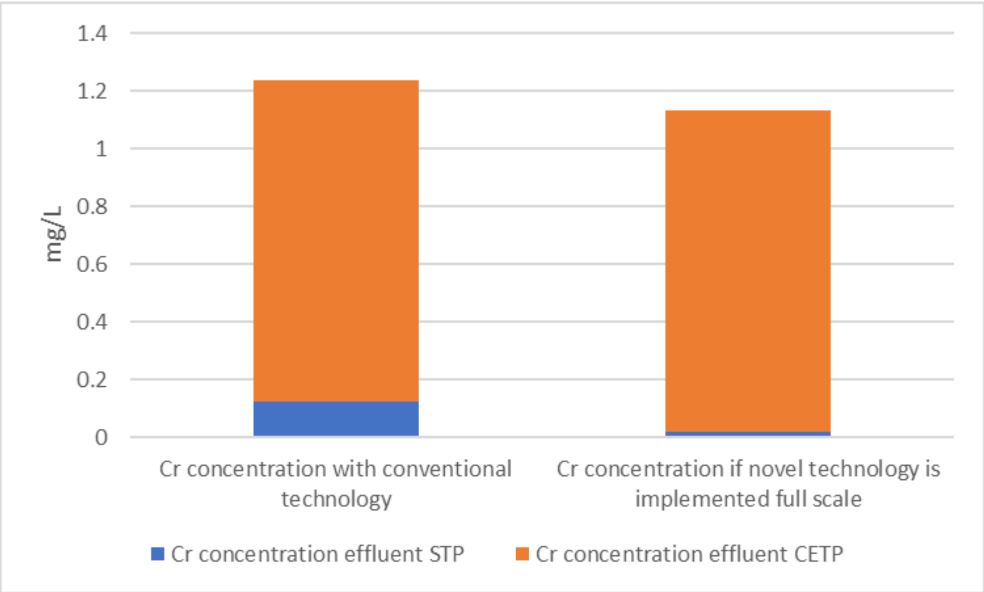
Hazardous event	Risks levels identified			
	Conventional ASP technology		Novel technology	
	Farmers	Children	Farmers	Children
Exposure during flood irrigation	high	high	high	high
Exposure during farming activities	high	high	high	high
Exposure through playing and helping parents on field	high	high	high	high
Exposure during preparation of contaminated crops	high	high	high	high

Exploring a hypothetical scenario with the average concentrations of total Cr in the STP effluent (S4), CETP effluent (S7) and CW+ effluent (S6) (Table 13/Section 4.2) Table 20 compares the current contribution of chromium of the STP and CETP to the mixed effluent and the projected contribution of chromium if the novel technology were implemented in full scale. Figure 20 shows that even when there is a chromium reduction of 84% in the STP effluent, the impact in the mixed STP+CETP would be only a slightly reduction of 8.4% in total Cr if there are no further changes in the CETP water quality regarding chromium.

Table 20. Comparison of chromium contributions to the mixed effluent STP and CETP

	Mean Cr concentration STP effluent (mg/L)	% STP in mixed effluent	Mean Cr concentration CETP effluent (mg/L)	% CETP in mixed effluent	Final Cr concentration mixed effluent (mg/L)
Conventional technology	0.19	65%	3.18	35%	(0.19*0.65) +(3.18*0.35) =1.24
If novel technology is implemented full scale	0.03	65%	3.18	35%	(0.03*0.65) + (3.18*0.35) =1.13

Figure 20. Comparison of the chromium concentration in the mixed effluent if the novel technology were implemented at full scale



Chapter 5. Conclusions

This chapter summarises the key findings of the study that aimed to explore the impact of a novel technology on the removal of chromium and the associated occupational health risk in Kanpur, India. It also addresses the research questions.

The 130 MLD Jajmau STP has a treatment train comprised of a screen chamber and grit removal (preliminary treatment), primary clarifier (primary treatment), ASP and secondary clarifier (secondary treatment). The sludge is treated in gravity thickener, and then mechanical dewatering or sludge lagoons. At the end, the sludge is transported to a storage/disposal site managed by the municipality. The effluent from the STP is mixed with the CETP effluent and used in the downstream villages to irrigate rice, wheat and paddy. The novel technologies implemented as pilots in the innovation site of the STP are IPC membrane and CW+.

The levels of total chromium discharging to the STP are extremely high and confirm the hypothesis of illegal discharges of tanneries to the STP. However, variability of chromium concentrations in the influent was not expected, and it could be related to working patterns of discharge in the tanneries.

The concentrations of hexavalent chromium, the most dangerous chromium species, were below 100µg/L. It was expected to find higher concentrations of hexavalent chromium in the wastewater, so it can be concluded that chromium is mainly present in the wastewater as trivalent chromium instead of hexavalent chromium, which represents a positive outcome since most of the occupation health risks are related to it. It also means that carcinogenic risk is lower for both STP workers and farmers reusing the effluent.

Though there is a high reduction of chromium levels during the treatment step, around 97% of the Cr concentration in the influent, the effluent of the STP does not comply with the maximum permissible limit of chromium for irrigation (0.1 mg/L). A noteworthy finding is that chromium is accumulated in the primary sludge, with extremely high concentrations of total Cr ranging from 8,672 to 16,532 mg/kg after the mechanical dewatering and in the sludge lagoons.

However, there was find hexavalent chromium levels in a range of 0.04 to 0.67 mg/kg in the sludge. This can represent an environmental concern regarding the disposal of highly chromium-concentrated sludge and a risk if the sludge is being reused in gardening activities or farming.

Another key finding was the current recirculation of the activated sludge, which seems to have impacted the accumulation of chromium within the treatment train in the aeration tank. This can pose an occupational risk for workers and affect the secondary treatment's efficiency.

For the STP workers using the conventional technology (E1), eight health risks related to chromium exposure were identified, mainly through skin contact. Three of them were assessed as high risk due to the high concentration of total chromium in the sludge and the presence of hexavalent chromium.

Health risks assessment for the farmers indicated four high health risks for the effluent reuse due to the high Cr concentrations in the mixed effluent STP+CETP. The CETP does not comply with the maximum permissible limit of chromium for irrigation (0.1 mg/L). A key finding is that the farmers' risk related to chromium exposure is predominantly coming from the CETP because its total Cr concentration is up to 16 times higher than the STP effluent. No significant change in the health risks will occur for the farmers reusing the effluent if there is no further reduction of chromium levels in the CETP effluent.

The theoretical impact of implementing the novel technology (IPC membrane and CW+) as a secondary treatment would reduce chromium concentrations in the effluent up to 6 times. However, since most chromium is accumulated in the sludge, it would not reduce the health risks associated with sludge management for STP workers. On the other hand, as the highest contribution of chromium for the irrigation water is coming from the CETP, swapping to the novel technology in the STP would not reduce the risk of farmers being exposed to highly chromium-concentrated mixed effluent.

Chapter 6. Limitations

This chapter presents some of the challenges faced during the research process, which constrained the extent of this study.

- The study was executed during monsoon season, which means that in general chromium concentrations would be more diluted that in other season.
- Some of the proposed sampling point were not sampled due to no access to sludge in the conventional technology and regarding the IPC membrane, the pilot had not produced enough sludge due to its short implementation.
- There were time limitations regarding the sampling, which set a limitation for assessing the variation of chromium concentration in the influent.
- Information regarding process sludge and quantities was only obtained trough KII with the STP Manager and there were no records to triangulate the data.

Chapter 7. Recommendations

This chapter presents some of the recommendations for future research.

- This study only considered occupational health risks hazards, so bioaccumulation of chromium in plants were not determined/
- The research only map the fate of sludge but did not deep into the storage/disposal site of the sludge and their potential reuse in gardening and other villages regarding high concentrations of chromium.
- Considering the high values of chromium in sludge, this research recommends future studies in chromium recovery from sludge.
- This research only determined chromium concentrations in sludge prior to disposal. Exploring chromium concentrations in the storage/disposal site would contribute to assess the posssibility of environmental transformations of trivalent chromium to hexavalent chromium.

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Appendices

Appendix A. - Research ethics declaration form

IHE DELFT Institute for Water Education under the auspices of UNESCO

Research Ethics Committee
IHE Delft Institute for
Water Education
E ResearchEthicsCommittee@un-ihe.org

Date:	2023-07-19
To:	Michelle Cedeño Villarreal
MSc Programme:	Water and Sustainable Development
Approval Number:	IHE-RECO 2023-kce001bwa03

Subject: Research Ethics approval

Dear Michelle,

Based on your application for Ethical Approval, the Research Ethics Committee (RECO) of IHE Delft RECO gives ethical clearance for your research topic "*The Fate of Chromium in Wastewater Treatment and Reuse, and the associated occupation health risks in Kanpur, India*".

This approval is valid until September 30, 2023.

The approval is based on the information submitted in the research ethics application form and endorsed by your mentor or supervisor. The approval of the Ethical Review Board concerns ethical aspects, as well as data management and privacy issues (including the GDPR). It should be noted that any changes in the research design oblige a renewed review by the Ethical Review Board.

Keep this letter for your records and include a copy of it in the final version of your MSc thesis, together with your personal ethics reflection.

On behalf of the Research Ethics Committee, I wish you success in the completion of your research.

Yours sincerely,

Dr. Emanuele Fantini
Coordinator, Research Ethics Committee IHE Delft

Copy to: Archive

Appendix B. - Participant information sheet

Participant Information Sheet

Dear Participant,

I am Michelle Cedeño Villarreal, an MSc student of IHE Delft Institute for Water Education. I am presently working on research titled: The Fate of Chromium in Wastewater Treatment and Reuse, and the associated occupation health risks in Kanpur, India.

Please take your time to read through the following information carefully. The aim is for you to be aware of the research purpose and what it involves before deciding to participate in an interview. If you have any questions or would like additional information, please feel free to ask the researcher.

Overview

The research project is a part of the Pavitra Ganga project, which aims to explore the impact of a novel technology on the removal of chromium and associated occupational health risks in Kanpur, India.

What have you been asked to do?

I am inviting you to participate in my MSc research study by participating in an anonymous and confidential interview session which will last for around 15-30 minutes. The research requires your opinions and current practices regarding wastewater treatment and reuse risks. Data obtained from you will only be used for the study and will not share with anyone outside our project team. Your participation is entirely voluntary, and you are not obliged to be a part of the interview. But I hope you will agree to participate since your opinions are essential. I will share the summary of my findings with you upon completion of the research. In case you need more information on the study, feel free to contact me on:

Contact information

Michelle Cedeño Villarreal
MSc. In Water and Sustainable Development IHE Delft Institute for Water Education
Westvest 7, 2611 AX Delft/ P.O.Box 3015, 2601 DA Delft
The Netherlands
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Kce001@un-ihe.org

Appendix C. - Consent of participation

Consent to take part in the fate of chromium in wastewater treatment and reuse, and the associated occupation health risks in Kanpur, India

The purpose of the study is to explore the impact of a novel technology on the removal of chromium and associated occupational health risks in Kanpur, India.

	Please check the box to show your agreement to the following points
I confirm that I have read and understood the information sheet for the above research. I have had the opportunity to read the information, ask questions and have had these answered satisfactorily.	☐
I agree that my participation is voluntary.	☐
I agree that I am free to withdraw at any moment.	☐
I agree that you contact me again to clarify any information.	☐
I consent to my have the session recorded and photographs taken	☐
I agree to take part in the interview.	☐

________________________ dd / mm / yyyy

Signature of participant Date

I believe the participant is giving informed consent to participate in this study

________________________ dd / mm / yyyy

Name of the Researcher Date

If you have any questions or concerns about the research, you can contact me on:
Michelle Cedeño Villarreal
MSc. In Water and Sustainable Development
IHE Delft Institute for Water Education, The Netherlands
+31 (0)645578794 - Kce001@un-ihe.org

Appendix D. - KII guides

KII Guide - STP MANAGER:

1. What is the treatment design capacity of the STP?

2. How is the sludge managed in the STP? What is the process to treat sludge in the STP? Could you describe it?
Probe: How is it treated or reused?
How and where is it disposed? How often is disposed the sludge?

3. What is the volume of wastewater that the STP treats per day?
What are the process flow parameters? L/day between one step to another one? What amount of each stream?
Influent flow (Volume per day):
Primary clarifier- aeration tank:
Aeration tank- secondary clarifier:
Effluent flow:
Probe: Do you have any records about the plant process flows that I can see?
Are there any specific control measures or monitoring systems in place to ensure efficient process flows?

4. Sludge Quantities: What is the volume/quantity of sludge produced by day/batch in the STP
Primary sludge:
Secondary sludge:
Return activated sludge:
Waste activated sludge:
Sludge dried in drying beds?
Probe: Are there any specific methods used to estimate the sludge production rate accurately?
Probe: What are the disposal methods for the sludge, and are there any regulations or guidelines governing its handling?
Probe: Have there been any initiatives or strategies implemented to minimize sludge production or improve its quality?

5. Sludge Retention Times: What is the average sludge retention time in your sewage treatment plant?
Probe: b) How is the retention time determined, and what factors influence its duration?
Probe: c) Are different retention times applied for primary and secondary sludge? If yes, why?
Probe: d) Have there been any recent changes or modifications in the sludge retention times, and if so, what were the reasons behind them?

6. What kind of health issues does your staff experience?
Probe: what are some of the safety measures put in place?

Appendix E. - Personal declaration

I, Karoll Michelle Cedeño Villarreal, declare that I have adhered to the principles of research ethics during this thesis on “The Fate of Chromium in Wastewater Treatment and Reuse, and the associated occupation health risks in Kanpur, India”. The results and discussion are executed by me. The Pavitra Ganga project contributed with the financial support for the fieldwork executed in Kanpur, India.

I worked with some field assistants during the data collection in the STP. I trained the field assistants on my research method. I obtained consent from the participants before carrying out practices such as note-taking and recording in the key interviews. I kept the subjects’ identities anonymous by using codes.

I developed this study under the mentorship of Dr Claire Furlong and the supervision of Prof. Tineke Hooijmans. I worked in the Civil and Environmental laboratory at IIT Kanpur under Prof. Purnendu Bose and I followed the standards of laboratory analysis and disposal of samples.

Ethical approval for this study was obtained from the IHE Delft Institute for Water Education research ethics committee (RECO).