Daughter of the mountains:
Final report of monitoring of surface and underground water in Medimurje and Zala county

A cross-border region where rivers connect, not divide

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Summary – EN

Geographically the Croatian and the Hungarian regions are divided by the Mura and Drava Rivers but both countries have the same water-related problems, thus it would be worth to observe the state of the international border rivers commonly. In case of the Mura monitoring system, there are already some information about hydrological, physical, chemical and biological parameters but the existing databases are insufficient. Furthermore, the information about the analytical, sample preparation and monitoring methods to determine the quality and quantity of these hazardous compounds are not summarized yet. The project will help to solve the above-mentioned problems for the specialists by creating a state review about occurrence of micropollutants in the Mura region, a sampling methodological plan including the state-of-the-art technologies and best practices, and an online platform for comprehensive dissemination.

There are various companies operating in the project area that can be sources of pollution for surface and groundwater.

By design of the Mura River monitoring, our goal was to monitor the chemical status of surface and groundwater and mapping the examination of the impact of effluent discharges or accidental pollution on the recipient under one-year period. In the case of surface waters, many components are analysed monthly (chemical and biological parameters, organic contaminants, drug residues) and the frequency of metals and pesticides determined in the other component groups varies. Metals are tested quarterly, while pesticides are also tested four times a year, but at different times. The definition of pesticides is scheduled for the spring months, as their releases to the environment are significant during this period.

The primary consideration in designating the surface sampling points was the location of the wastewater treatment plant. When designating the sampling points, we took into account the potential vulnerabilities arising from human interventions and activities on both the Croatian and Hungarian sides. In the examined section (approx. 50 km), sampling points were designated in connection with 7 settlements, mainly in connection with the points of discharge of treated wastewater from a given settlement into the receiver.

In the examined section, the surface water temperature changed according to the season, while the temperature of the underground water was roughly balanced during the one-year period. During the sampling period, the dissolved oxygen values measured in a given river section showed adequate levels. The measured biological oxygen demand values from the Mura River do not show significant changes after the intake points. The legal limit for surface water is not exceeded at any of the sampling points. The data show that the chemical oxygen demand of

water discharged at three sites is quite high, but this value decreases rapidly as it is diluted. These values can be caused by inadequate treatment of wastewater or abnormal operations of wastewater treatment plants, perhaps in some cases the chlorine content of the samples was high at the time of the measurements, which affected the results. These high discharges can be most dangerous in drier periods when higher concentrations remain after discharge into the river. The total organic carbon results show a high value for one location, which is normalised at the point after the inflow. This could be caused by organic matter enriched at the measurement point and diluted to the post-inflow measurement point. In most cases parallels can be drawn between total organic carbon and chemical oxygen demand results, in this case this can be fully said.

In the case of turbidity, no correlation can be established between the values of the water of the river and the tributaries. In the case of conductivity, it can be established that the values measured at the sewage inlets on the Mura River were higher than in the river water, which is due to the ionic content of the treated sewage. In the case of the pH values, it can be determined that they varied between 7.5 and 8.5, which fall into the slightly alkaline range.

The data clearly show that ammonium concentrations are extremely high at three of the inflow points and then fall rapidly once the ammonium is discharged into the river. Based on the present study, the higher ammonium concentrations in the inflow did not have a serious impact on the river, but in the longer term and during drier periods they may cause eutrophication, which could seriously damage aquatic life. Based on the measured data, the water quality meets EU requirements. In case of phosphorus four inflow points had particularly high concentrations. Contamination of heavy metals in the aquatic environment has attracted global attention owing to its abundance, persistence and environmental toxicity. Molnári 1 (Vicsa creek) point is outstanding, where the iron and manganese concentrations were extremely high. Mercury concentrations were below 1.5 μg/l in surface and underground waters (with the exception of one: ~4 μg/l). The concentration of arsenic in surface waters was below 3 μg/l. In the case of groundwater, it can be said that on the Hungarian side they were below 4 μg/l, while on the Croatian side it was almost undetectable.

During the survey, we did not experience any outliers or exaggerated values during the examination organic components. Taking seasonal applications into account, we expected temporal variations in the case of pesticides. However, this was not observed in the case of total pesticides. In this survey the most frequently detected pharmaceutical was diclofenac, estrogenic ethynil-estradiol was detected in more than half of the samples, while naproxen was also detected at the same time. It was found that wastewater treatment plant effluents contain

significant amounts of pharmaceuticals. The wastewater treatment plant loads have a possible major role on the drug contamination of the studied area.

Összefoglaló - HU

A horvát és a magyar régiót földrajzilag a Mura és a Dráva osztja ketté, de mindkét ország vízügyi problémái azonosak, ezért érdemes közösen tanulmányozni a nemzetközi határfolyók állapotát. A Mura monitoring rendszer esetében már van némi információ a hidrológiai, fizikai, kémiai és biológiai paraméterekről, de a meglévő adatbázisok nem elegendőek. Ezen kívül a veszélyes vegyületek minőségének és mennyiségének meghatározására szolgáló analitikai, minta-előkészítési és monitorozási módszerekről szóló információk még nincsenek összefoglalva. A projekt a fent említett problémák megoldását segíti a szakemberek számára a Mura régióban előforduló mikroszennyező anyagok állapotfelmérésével, a legmodernebb technológiákat és legjobb gyakorlatokat tartalmazó mintavételi módszertani terv elkészítésével, valamint egy online platformmal.

A projekt területén különböző cégek működnek, amelyek felszíni és felszín alatti vizek szennyező forrásai lehetnek.

A Mura folyó monitoring tervezésével célunk volt a felszíni és felszín alatti vizek kémiai állapotának monitorozása, valamint a szennyvízkibocsátások vagy véletlen szennyezések befogadóra gyakorolt hatásának feltérképezése egy éves időtartam alatt. A felszíni vizek esetében számos komponens elemzése havonta történik (kémiai és biológiai paraméterek, szerves szennyeződések, gyógyszermaradványok), a többi komponenscsoportban a fémek és növényvédő szerek meghatározott gyakorisága változó. A fémeket negyedévente, a növényvédő szereket szintén évente négyszer, de eltérő időpontokban vizsgáltuk. A növényvédő szerek meghatározását a tavaszi hónapokra terveztük, mivel ebben az időszakban jelentős a környezetbe való kibocsátásuk.

A felszíni mintavételi helyek kijelölésénél elsődleges szempont a szennyvíztisztító telepek elhelyezkedése volt. A mintavételi helyek kijelölésénél figyelembe vettük az emberi beavatkozásokból és tevékenységből adódó potenciális szennyező forrásokat a horvát és magyar oldalon egyaránt. A vizsgált szakaszon (kb. 50 km) 7 településhez kapcsolódóan kerültek kijelölésre mintavételi pontok, elsősorban az adott településről származó tisztított szennyvíz befogadóba történő bevezetési helyeihez kapcsolódóan.

A vizsgált szakaszon a felszíni víz hőmérséklete az évszaknak megfelelően változott, míg a felszín alatti vizek hőmérséklete nagyjából kiegyensúlyozott volt az vizsgált időtartam alatt. A mintavételi időszakban az adott folyószakaszon mért oldott oxigén értékek megfelelő szintet mutattak. A Mura folyóból mért biokémiai oxigénigény értékek nem mutatnak szignifikáns változást a befolyó pontok után. A felszíni vizekre vonatkozó törvényi határértéket egyik mintavételi hely sem lépte túl. Az adatok azt mutatják, hogy a három helyen kibocsátott víz

kémiai oxigénigénye meglehetősen magas volt, de ez az érték a felhígulással gyorsan csökkent. Ezeket az értékeket a szennyvíz nem megfelelő tisztítása vagy a szennyvíztisztító telepek rendellenes működése okozhatja, esetleg egyes esetekben a minták magas klórtartalma. Ezek a nagy vízhozamok a szárazabb időszakokban lehetnek a legveszélyesebbek, amikor a folyóba való kibocsátás után magasabb koncentrációk adódnak. Az összes szerves szén egy helyen magas értéket mutatott, amely a beáramlás utáni ponton normalizálódott. Ezt okozhatja a mérési ponton feldúsult és a beáramlás utáni mérési pontig hígított szerves anyag. A legtöbb esetben párhuzam vonható az összes szerves szén és a kémiai oxigénigény értékei között, mely ebben az esetben is teljes mértékben elmondható.

Zavarosság esetén a folyó és a befolyók vizének értékei között összefüggés nem volt megállapítható. A vezetőképesség esetében megállapítható, hogy a Mura folyón a szennyvízbevezetéseknél mért értékek magasabbak voltak, mint a folyóvízben, ami a tisztított szennyvíz iontartalmának köszönhető. A pH-értékek esetében megállapítható, hogy 7,5 és 8,5 között változtak, ami az enyhén lúgos tartományba esik.

Az adatok egyértelműen azt mutatják, hogy az ammónium-ion koncentráció három beáramlási ponton rendkívül magas volt, majd gyorsan csökkent ahogy a folyóba került, hiszen azonnal oxidálódott a magas oxigénkoncentrációjú folyóvízben. Jelen tanulmány alapján a befolyók magasabb ammónium-ion koncentrációi nem gyakoroltak komoly hatást a folyóra, de hosszabb távon és szárazabb időszakokban eutrofizációt okozhatnak, ami súlyosan károsíthatja a vízi élővilágot. A mért adatok alapján a víz minősége megfelel az EU követelményeinek. A foszfor esetében négy beáramlási ponton volt különösen magas a koncentráció.

A vízi környezetben világszerte előforduló nehézfémszennyezések perzisztenciájuk és környezeti toxicitásuk miatt felkeltették a figyelmet. Kiemelkedő a Molnári 1 (Vicsa patak) pont, ahol a vas és a mangán koncentrációja rendkívül magas volt. A higanykoncentráció 1,5 μg/l alatt volt a felszíni és felszín alatti vizekben (egy kivételével: ~4 μg/l). A felszíni vizekben az arzén koncentrációja 3 μg/l alatt volt. A talajvíz esetében elmondható, hogy az értékek a magyar oldalon 4 μg/l alatt voltak, míg a horvát oldalon szinte nem voltak kimutathatók.

A felmérés során a szerves komponensek vizsgálatánál nem tapasztaltunk kiugró értékeket. A szezonális alkalmazásokat figyelembe véve a növényvédő szerek esetében időbeli eltérésekre számítottunk. Ez azonban nem volt megfigyelhető az összes peszticid esetében. A leggyakrabban kimutatott gyógyszer a diklofenak volt, a minták több mint felében etinil-ösztradiol, valamint naproxen is kimutatható volt. Megállapítást nyert, hogy a szennyvíztisztító telepek szennyvizei jelentős mennyiségű gyógyszert tartalmaznak. A szennyvíztisztító telepi terheléseknek nagy szerepe lehet a vizsgált terület gyógyszermaradványokkal történő szennyezettségében.

Sažetak – HR

Hrvatsko i mađarsko pogranično područje geografski dijele Mura i Drava, ali problemi s vodom u obje zemlje su isti, stoga je vrijedno zajednički proučavati stanje međunarodnih graničnih rijeka. U slučaju monitoring sustava Mure već postoje podaci o hidrološkim, fizikalnim, kemijskim i biološkim parametrima, ali postojeće baze podataka nisu dostatne. Osim toga, podaci o analitičkim metodama, metodama pripreme uzoraka i praćenja za određivanje kvalitete i količine opasnih spojeva još nisu sažeti. Projekt pomaže stručnjacima u rješavanju navedenih problema procjenom stanja mikroonečišćujućih tvari u regiji Mura, izradom plana metodologije uzorkovanja koji uključuje najsuvremenije tehnologije i najbolju praksu te online platformom. Na projektnom području djeluju različite tvrtke koje mogu biti izvori onečišćenja površinskih i podzemnih voda.

Planiranjem monitoringa rijeke Mure cilj nam je bio pratiti kemijsko stanje površinskih i podzemnih voda, te kartirati utjecaj ispuštanja otpadnih voda ili akcidentnog onečišćenja na recipijent u jednogodišnjem razdoblju. U slučaju površinskih voda mjesečno se analizira više komponenti (kemijski i biološki parametri, organska onečišćenja, ostaci lijekova), u ostalim skupinama komponenata navedena učestalost metala i sredstava za zaštitu bilja varira. Metali su ispitivani tromjesečno, a sredstva za zaštitu bilja također četiri puta godišnje, ali u različito vrijeme. Određivanje sredstava za zaštitu bilja planirano je u proljetnim mjesecima jer je u tom razdoblju njihovo ispuštanje u okoliš dosta značajno.

Lokacija postrojenja za pročišćavanje otpadnih voda bila je primarni faktor u odabiru mjesta površinskog uzorkovanja. Prilikom odabira mjesta uzorkovanja uzeli smo u obzir potencijalne izvore onečišćenja uzrokovane ljudskim intervencijama i aktivnostima i s hrvatske i s mađarske strane. Na ispitivanoj dionici (cca. 50 km) određena su mjesta uzorkovanja vezana za 7 naselja, prvenstveno vezano uz točke uvođenja pročišćenih otpadnih voda iz navedenog naselja u prihvatni objekt.

U ispitivanom dijelu temperatura površinske vode mijenjala se ovisno o godišnjem dobu, dok je temperatura podzemne vode bila približno uravnotežena tijekom ispitivanog razdoblja. Tijekom perioda uzorkovanja, vrijednosti otopljenog kisika izmjerene u određenom dijelu rijeke pokazale su odgovarajuću razinu. Vrijednosti biokemijske potrošnje kisika izmjerene iz rijeke Mure ne pokazuju značajne promjene nakon točaka utoka. Niti jedno mjesto uzorkovanja nije premašilo zakonsku granicu površinskih voda. Podaci pokazuju da je kemijska potreba za kisikom u vodi ispuštenoj s tri lokacije bila prilično visoka, ali je ta vrijednost brzo opadala s razrjeđivanjem. Ove vrijednosti mogu biti uzrokovane neadekvatnim čišćenjem otpadnih voda ili nenormalnim radom uređaja za pročišćavanje otpadnih voda, ili u nekim slučajevima

visokim sadržajem klora u uzorcima. Ovi visoki protoki mogu biti najopasniji tijekom sušnih razdoblja kada se veće koncentracije javljaju nakon ispuštanja u rijeku. Ukupni organski ugljik pokazao je visoku vrijednost na jednom mjestu, koja se normalizirala na točci nakon ulaska. To može biti uzrokovano organskom tvari obogaćenom na točki mjerenja i razrijeđenom do točke mjerenja nakon dotoka. U većini slučajeva može se povući paralela između vrijednosti cjelokupnog organskog ugljika i kemijske potrebe za kisikom, što se i u ovom slučaju može u potpunosti navesti.

U slučaju mutnoće nije se mogla uspostaviti korelacija između vrijednosti vode rijeke i pritoka. U slučaju vodljivosti može se utvrditi da su izmjerene vrijednosti na kanalizacijskim ulazima rijeke Mure veće nego u riječnoj vodi, što je posljedica ionskog sadržaja pročišćene otpadne vode. Kod pH vrijednosti može se utvrditi da su varirale između 7,5 i 8,5, što je u blago lužnatom području. Podaci jasno pokazuju da je koncentracija amonijevih iona bila iznimno visoka na tri točke dotoka, a zatim je brzo opadala kako je ulazio u rijeku, budući da je odmah oksidiran u riječnoj vodi s visokom koncentracijom kisika. Na temelju ove studije, veće koncentracije amonijevih iona u dotocima nisu imale ozbiljan učinak na rijeku, ali dugoročno iu sušnijim razdobljima mogu izazvati eutrofikaciju, što može ozbiljno oštetiti vodeni svijet. Na temelju izmjerenih podataka kvaliteta vode zadovoljava zahtjeve EU. Kod fosfora je koncentracija bila posebno visoka na četiri ulazne točke.

Zbog njihove postojanosti i toksičnosti za okoliš, onečišćenje teškim metalima koje se događa u vodenom okolišu diljem svijeta privuklo je pozornost. Ističe se točka Molnári 1 (Vicsa patak) gdje je koncentracija željeza i mangana bila izrazito visoka. Koncentracija žive bila je ispod 1,5 µg/l u površinskim i podzemnim vodama (s jednom iznimkom: ~4 µg/l). Koncentracija arsena u površinskim vodama bila je ispod 3 µg/l. U slučaju podzemnih voda, može se reći da su vrijednosti bile ispod 4 µg/l s mađarske strane, dok su s hrvatske strane bile gotovo nemjerljive i nezanemarive.

Tijekom istraživanja nisu primijećeni odstupanja u ispitivanju organskih komponenti. Uzimajući u obzir sezonske primjene, očekivali smo vremenske razlike u slučaju sredstava za zaštitu bilja. Međutim, to nije uočeno za sve pesticide. Najčešće detektirani lijek bio je diklofenak, a u više od polovice uzoraka također su detektirani etinilestradiol i naproksen. Utvrđeno je da otpadne vode iz uređaja za pročišćavanje otpadnih voda sadrže značajne količine lijekova. Opterećenje uređaja za pročišćavanje otpadnih voda može igrati veliku ulogu u kontaminaciji istraživanog područja ostacima lijekova.

1. Project summary

Europe has a great chance in the water research and management since the idea and the necessity of reuse of world water resources is not only a local but also a global task. Actually, the Middle European region is not ready for the export of knowledge to other countries, because the local companies and experts have not enough skills to cooperate and share their experiences in these essential topics.

It is important for the national organizations to have appropriate orientation. For achieving the good quality of water bodies, the local governments, researchers, industrial specialists and all citizens in their own territory have to cooperate. The goal is to share knowledge, information and the good practices among the parties.

The European Community recognized that the drinking water supply of the growing population and service systems represent huge economic, scientific and technological tasks. Therefore, the European Commission (EC) created the Water Framework Directive (2000/60/EC) with the goal of "achieving a 'good status' for all of Europe's surface waters and groundwaters by 2015", where 'good status' means "good ecological and chemical status in terms of low levels of chemical pollution as well as a healthy ecosystem". With the created Water Framework Directive the goal is to establish a legal framework to protect and restore clean water across Europe and ensure its long-term, sustainable use. With the "watch list" the EC has determined 45 priority substances in the 213/39/EU European Union Directive. According to the latest scientific results, it would be necessary to add some other compounds such as non-steroidal anti-inflammatory substances and their metabolites to this list, while they could represent risks to human and environmental health in case of long-term exposure.

In the current stage, Europe is going to collect information about the quality of surface and groundwaters with priority substances. Since the waters do not know the borders, the challenges are the same in every affected country in respect of reaching and preserving the good status of waters.

Handling these topics in cross-border cooperation could be a good example for the further international collaborations. Geographically the Croatian and the Hungarian regions are divided by the Mura and Drava Rivers but both countries have the same water-related problems, thus it would be worth to observe the state of the international border rivers commonly. In case of the Mura monitoring system, there are already some information about hydrological, physical, chemical and biological parameters but the existing databases are insufficient especially about priority substances. Furthermore, the information about the analytical, sample preparation and monitoring methods to determine the quality and quantity of these hazardous compounds are

not summarized yet. The project will help to solve the above-mentioned problems for the specialists by creating a state review about occurrence of micropollutants in the Mura region, a sampling methodological plan including the state-of-the-art technologies and best practices, and an online platform for comprehensive dissemination. These new collections can be put into the practice and can develop a well-working cross-border network for improving water quality.

It is necessary to connect the specialist and create professional groups for the information exchange, because everywhere in the border region of both countries many research groups, institutes and companies are involved in the water management and water treatment, but they are working separately and there is a lack of efficient dissemination of information. This network could be expanded in the near future on the whole European region and could help to achieve the good status of water bodies.

Mura is a cross-border river in Central Europe which connects four countries with its 465 km length. It is a tributary of the Drava and subsequently the Danube. The size of its basin is 14,304 km^2. The Landscape Conservation Area along the Mura extends from the estuary of the Kerka to the Drava and includes the area from the border to the south-western edge of the Zala Hills. After hundreds of years of constant cultivation, due to military closures it has regained its natural character, however these habitats require further monitoring and management.

The rivers Mura and Drava geographically divide the Croatian and Hungarian regions. As both countries have the same problems with surface and groundwater, it is advisable to jointly map the state of the border rivers. This Interreg project (HUHR/1901/2.2.1/01289) is intended to identify and solve problems for professionals by provide detection of current contaminants in a wide range. This process consists of developing a sampling methodology plan using state-of-the-art technologies and best practices, providing an overview of the occurrence of water pollutants in the Mura region, and operating an online platform to disseminate the results more widely. Utilizing the principles of Interreg programmes (e.g., efficiency, effectiveness, interregional learning, cooperation) the main goal is to develop a regional research network system through joint cooperation and professional cooperation in the region, thus collecting and sharing information obtained during water sampling in order to protect the aquatic environment of the transboundary region with experts in the water sectors. The most significant aim of this study was 1) to characterize River Mura on the basis of the literature search prior to the start of the work, to explore the characteristics and sources of pollution of the studied area, thus, designate the analytes should be examined, in addition 2) to develop a comprehensive sampling plan that takes into account the most important pollutant sources and to set up a comprehensive monitoring network of Mura River (focused on water quality). Water pollution has a significant impact on the natural renewal of water resources. Pollution does not know the concept of

national borders! Pollutants transported in rivers can cross regional and national borders and eventually reach the ocean, where they can spread uncontrollably. Diffuse pollution from landfills or agricultural sources, as wastes, fertilizers and pesticides are mainly non-point sources, however, treated industrial and municipal wastewater discharges are point sources. All the water is eventually used in the natural cycle and contains detectable amounts of various chemicals. Untreated municipal wastewater contains a number of components, from dissolved metals and organic compounds to large solids such as rags, sticks, floating objects, granules and greases. Inorganic constituents of wastewater include metals, salts, oxyhalides, nutrients and potentially engineered nanomaterials. The organic composition of raw wastewater includes naturally occurring humic substances, faecal matter, kitchen waste, liquid detergents, oils, greases, consumer goods, industrial waste and other substances that become part of the wastewater. The former wastewater treatment technologies had to be developed and supplemented with new procedures in order to prevent pollution and damage to the environment. Sophisticated analytical tools allow the identification and quantification of extremely low levels of each inorganic and organic constituent. The danger is mainly the dissolved contaminant, which can easily be absorbed into the food chain, accumulate in organisms and have an adverse, harmful effect. In addition, heat is a source of pollution if it changes the properties of the water in an unfavourable direction for the living world.

In European Union the monitoring of river water quality is carried out on the basis of laws and regulations in accordance with the requirements of the Water Framework Directive (WFD - Directive 2000/60/EC) and other guidelines and professional instructions for the establishment and implementation of the monitoring. The Directive determines the limit values of parameters and criteria for the assessment of the chemical status. In recent years, monitoring of anthropogenic pollutants in surface water have been emphasized not only in media but also in legal activity in European Union. Hormones, antibiotics, pesticides, antidepressants, anti-epileptic drugs and analgesics come to spotlight with the EU Priority Substance Watch List (WL, 2018/840) of surface water (under Water Framework Directive, renew in 2018). Monitoring of these substances in surface water is mandatory for each member state.

In general, pollution is made up of municipal, industrial, agricultural and diffuse sources. Industrial activities release significant amounts of wastewater into the environment, almost all of which end up in surface waters. In the agricultural sector, intensive farming, combined with high use of fertilizers and pesticides, has led to the pollution of groundwater with nitrates and pesticides. Large livestock farms are significant point sources of water pollution, with rudimentary wastewater treatment posing a particular risk in karst and groundwater near small streams. In the case of toxic substances (metals, pesticides, organic compounds), industry

accounts for more than half of the pollutants, while municipal and agricultural sources account for the rest. Landfills are one of the main sources of untreated leachate, which can have a potentially severe impact on groundwater and surface water.

There are various companies operating in the project area that can be sources of pollution for surface and groundwater. The most important sources of pollution in the Hungarian project area are abandoned illegal landfills, illegally drilled wells, gas stations, plants, sewage plants, railway lines, thermal baths, and diffuse pollution of intensively cultivated areas, which involves the use of fertilizers and pesticides. The latter is ubiquitous in the project area and, for some parameters, can have a major impact on the quality of surface water and groundwater. The main sources of pollution in Croatia in the study area are meat- and textile industry, industrial laundry, hospitals, car maintenance, metal industry, car- and food industry, manufacture of bricks, ceramics and glass.

Taking the above into account, the selected component groups of the monitoring are the following: metals, chemical parameters, organic components, pharmaceuticals, herbicides/pesticides, biological parameters. Currently, the most commonly used method for measuring levels of chemical pollutants is spot (bottle) sampling, followed by extraction and instrumental analysis. This methodology is well established and validated, so it has been accepted for regulatory and legislation purposes. One of the main difficulties in sampling is preservation (handling and storage) of the sample. The initial composition of the sample must be maintained from sampling through to analysis. If this is not the case, the final conclusions will not reflect the initial situation. Water-sampling strategy and select of sampling location are important during status survey of water environment. The sampling site should represent the environment under study. Criteria for section allocation is the two-level point allocation: at a specified river section (around pollution source input) the same number of sampling points (before – after) should be sampled. The primary consideration in designating the surface sampling points was the location of the wastewater treatment plant. When designating the sampling points, we took into account the potential vulnerabilities arising from human interventions and activities on both the Croatian and Hungarian sides. In the examined section (approx. 50 km), sampling points were designated in connection with 7 settlements, mainly in connection with the points of discharge of treated wastewater from a given settlement into the receiver.

By design of the Mura River monitoring, our goal was to monitor the chemical status of surface and groundwater and mapping the examination of the impact of effluent discharges or accidental pollution on the recipient under one-year period. In the case of surface waters, many components are analysed monthly (chemical and biological parameters, organic contaminants,

drug residues) and the frequency of metals and pesticides determined in the other component groups varies. Metals are tested quarterly, while pesticides are also tested four times a year, but at different times. The definition of pesticides is scheduled for the spring months, as their releases to the environment are significant during this period.

2. Sampling locations and methods

The primary consideration in designating the surface sampling points was the location of the wastewater treatment plant. When designating the sampling points, we took into account the potential vulnerabilities arising from human interventions and activities on both the Croatian and Hungarian sides. In the examined section (approx. 50 km), sampling points were designated in connection with 7 settlements, mainly in connection with the points of discharge of treated wastewater from a given settlement into the receiver. Three points were designated at each site (under the influence of wastewater, in front of and after it). An exception to this was the Letenye point, where the treated wastewater is not introduced in surface water, but through a discharge pipe. At 14 points, sampling takes place directly from the line of the Mura River.
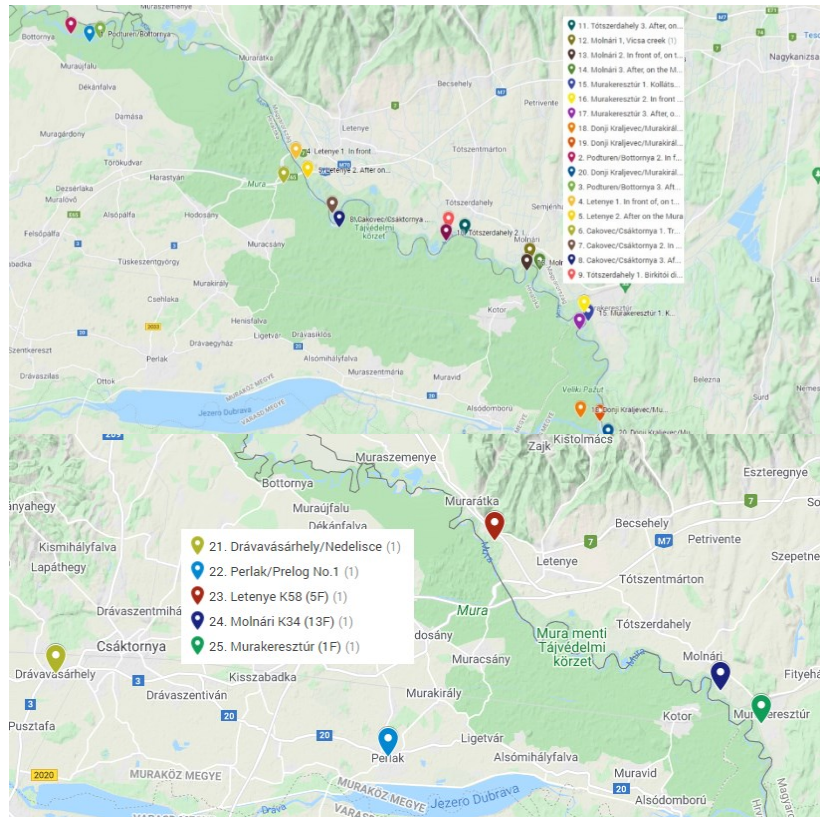
The sampling points of surface and underground waters

			Sampling points		
WWTPs from northwest to southeast along the Mura River			**In front of the inflow point into the Mura River**	**In front of the inflow point on the Mura River**	**After the inflow point on the Mura River**
A	Croatia	Bottornya / **Podturen**	1.	2.	3.
B	Hungary	**Letenye** / Letinja	-	4.	5.
C	Croatia	Csáktornya / **Čakovec**	6.	7.	8.
D	Hungary	**Tótszerdahely** / Serdahelj	9.	10.	11.
E	Hungary	**Molnári** / Mlinarci	12.	13.	14.
F	Hungary	**Murakeresztúr** / Kerestur	15.	16.	17.
G	Croatia	Murakirály / **Donji Kraljevec**	18.	19.	20.

Monitoring wells in the nearby environment of the Mura River			**Sampling points**
H	Croatia	Drávavásárhely / **Nedelisce**	21.
I	Croatia	Perlak / **Prelog**	22.
J	Hungary	**Letenye** /Letinja	23.
K	Hungary	**Molnári** /Mlinarci	24.
L	Hungary	**Murakeresztúr** /Kerestur	25.

The designated sampling dates (12 days during the whole year period) were as follows: 8th, June 2021; 6th, July 2021; 3rd, August 2021; 7th, September 2021; 5th, October 2021; 2nd, November 2021; 7th, December 2021; 7th, January 2022; 16th, March 2022; 5th, April 2022; 5th, May 2022; 31st, May 2022.

Among the physical and chemical parameters, water temperature, dissolved oxygen, pH, conductivity, total P, total N, nitrate, nitrite, ammonium, chemical oxygen demand, biochemical oxygen demand, total organic carbon and hydrocarbons were examined. For metals, iron, manganese, cadmium, copper, lead, mercury and arsenic were measured. Concentrations of organic components, insecticides and certain drug residues were also measured, and microbiological tests were performed.

The frequency of the measurements

Name of analyte	Component group	Total measurements	Frequency of measurements
iron	Metals	100	4/year
manganase	Metals	100	4/year
cadmium	Metals	100	4/year
copper	Metals	100	4/year
lead	Metals	100	4/year
mercury	Metals	100	4/year
arsenic	Metals	100	4/year
turbidity	Chemical parameters	252	12/year
sulfate	Chemical parameters	252	12/year
cianide	Chemical parameters	252	12/year
boron	Chemical parameters	252	12/year
pH	Chemical parameters	252	12/year
conductivity	Chemical parameters	252	12/year
total P	Chemical parameters	252	12/year
Kjeldal N/ total N	Chemical parameters	252	12/year
NO_3	Chemical parameters	252	12/year
NO_2	Chemical parameters	252	12/year
NH_3	Chemical parameters	252	12/year
BOD	Chemical parameters	252	12/year
COD	Chemical parameters	252	12/year
dissolved oxygen	Chemical parameters	252	12/year
TOC	Chemical parameters	252	12/year
CH	Chemical parameters	252	12/year
total PAH	Organic components	235	12/year
total PCBs	Organic components	235	12/year
total THM	Organic components	235	12/year
benzene/ benzol	Organic components	235	12/year
total pesticides	Pesticides	100	4/year
diclofenac	Pharmaceuticals	252	12/year
naproxen	Pharmaceuticals	252	12/year
ethynil-estradiol	Pharmaceuticals	252	12/year
Hexabromocyclododecane	Flame retardant	100	4/year
Coliform	Microbiology	252	12/year
Escherichia coli	Microbiology	252	12/year
Enteroccus	Microbiology	252	12/year
colony count 22°C	Microbiology	252	12/year

The used methods and analizator types

Name of analyte	Sampling method		Analytical method	Analizator type
iron	MSZ 21464:1998(v.sz)	MSZ ISO 5667-6:1995	MSZ 1484-3:2006 Chapter 6	ConntrAA 300 Continuum Source Atomic Absorption Spectrometer
manganase	MSZ 21464:1998(v.sz)	MSZ ISO 5667-6:1995	MSZ 1484-3:2006 Chapter 6	ConntrAA 300 Continuum Source Atomic Absorption Spectrometer
cadmium	MSZ 21464:1998(v.sz)	MSZ ISO 5667-6:1995	MSZ 1484-3:2006 Chapter 6	ConntrAA 300 Continuum Source Atomic Absorption Spectrometer
copper	MSZ 21464:1998(v.sz)	MSZ ISO 5667-6:1995	MSZ 1484-3:2006 Chapter 6	ConntrAA 300 Continuum Source Atomic Absorption Spectrometer
lead	MSZ 21464:1998(v.sz)	MSZ ISO 5667-6:1995	MSZ 1484-3:2006 Chapter 6	ConntrAA 300 Continuum Source Atomic Absorption Spectrometer
mercury	MSZ 21464:1998(v.sz)	MSZ ISO 5667-6:1995	MSZ EN 13506:2002	Mercur
arsenic	MSZ 21464:1998(v.sz)	MSZ ISO 5667-6:1995	MSZ 1484-3:2006 Chapter 7	ZEEnit 650 Atomic absorption Spectrometer
turbidity	HRN EN ISO 5667-6		HRN EN ISO 7027:2001	Portable Turbidimeter 2100Qis
sulfate	HRN EN ISO 5667-6		HRN EN ISO 10304-1:2009	IC
cianide	HRN EN ISO 5667-6		HRN ISO 6703-2:2001 (ISO 6703-2:1984)	Spectrometer
boron	HRN EN ISO 5667-6		HRN EN ISO 11885:2010 (ISO 11885:2007, EN ISO 11885:2009)	ICP-OES
pH	HRN EN ISO 5667-6		HRN ISO 10523:2012	WTW Multimeter 740, pH-electrode SenTix 81
conductivity	HRN EN ISO 5667-6		HRN ISO 7888:2001	WTW Multimeter 740, TetraCon 325 electrode
total P	HRN EN ISO 5667-6		HRN ISO 6878:2001	Spectrophotometer, Hach, DR 6000
Kjeldal N/ total N	HRN EN ISO 5667-6		Modified EN ISO 11905-1:1997, Method with small closed tubes	Spectrophotometer, Hach, DR 6000
NO$_3$	HRN EN ISO 5667-6		Standard Methods 4500-NO3-B	Spectrophotometer, Hach, DR 6000
NO$_2$	HRN EN ISO 5667-6		In-house method according to "Voda za piće - standardne metode za ispitivanje higijenske ispravnosti", Beograd, 1990.	Spectrophotometer, Hach, DR 6000
NH$_3$	HRN EN ISO 5667-6		HRN ISO 7150-1:1998	Spectrophotometer, Hach, DR 6000
BOD	HRN EN ISO 5667-6			WTW OxiTop - Manometric BOD Measuring Devices, HACH - BOD-System
COD	HRN EN ISO 5667-6		HRN ISO 15705-1:2003	Spectrophotometer, Hach, DR 6000
dissolved oxygen	HRN EN ISO 5667-6			HACH HQ440d-Multi-parameter, LDO101 probe
TOC	HRN EN ISO 5667-6		HRN EN ISO 1484:2002	TOC analyser
CH	HRN EN ISO 5667-6		HRN EN ISO 9377-2:2002	
total PAH			MSZ 1484-6:2003	GC-MS
total PCBs			EPA 8082A:2007	GC-MS/MS
total THM	MSZ 21464:1998(v.sz)	MSZ ISO 5667-6:1995	MSZ 1484-4:1998	HS-GC-MS
benzene/ benzol	MSZ 21464:1998(v.sz)	MSZ ISO 5667-6:1995	MSZ 1484-5:1998	HS-GC-MS
total pesticides			EPA 8141B:2007; MSZ EN ISO 10695:2000; EPA 8270E:2018; EPA 8151A:1996; ISO 16308:2014; EPA 1656A:2000	GC-MS/MS; HPLC-MS/MS
diclofenac			Commission implementing decision (EU) 2018/840	SPE-LC-MS/MS
naproxen			Commission implementing decision (EU) 2018/840	SPE-LC-MS/MS
ethynil-estradiol			Commission implementing decision (EU) 2018/840	SPE-LC-MS/MS
Hexabromocyclododecane			ÁM-145:2017	HPLC_MS/MS
Coliform				
Escherichia coli				
Enteroccus				
colony count 22°C				

Limit of Detection (LOD), and Limit of Quantitation (LOQ)

Name of analyte	Component group	LOD	Unit LOD	LOQ	Unit LOQ
iron	Metals	50	µg/l	50	µg/l
manganase	Metals	10	µg/l	10	µg/l
cadmium	Metals	50	µg/l	50	µg/l
copper	Metals	50	µg/l	50	µg/l
lead	Metals	50	µg/l	50	µg/l
mercury	Metals	0.1	µg/l	0.1	µg/l
arsenic	Metals	0.5	µg/l	0.5	µg/l
turbidity	Chemical parameters				
sulfate	Chemical parameters	5	mg/l	5	mg/l
cianide	Chemical parameters	0.01	mg/l	0.01	mg/l
boron	Chemical parameters	5	µg/l	5	µg/l
pH	Chemical parameters				
conductivity	Chemical parameters				
total P	Chemical parameters	0.0065	mg/l P	0.02168	mg/l P
Kjeldal N/ total N	Chemical parameters	0.0727	mg/l N	0.2423	mg/l N
NO_3	Chemical parameters	0.00155	mg/l N	0.00516	mg/l N
NO_2	Chemical parameters	0.00274	mg/l N	0.00548	mg/l N
NH_3	Chemical parameters	0.00671	mg/l N	0.02236	mg/l N
BOD	Chemical parameters				
COD	Chemical parameters	3.5	mg/l O_2	11.6	mg/l O_2
dissolved oxygen	Chemical parameters				
TOC	Chemical parameters	0.188	mg/l	0.188	mg/l
CH	Chemical parameters	0.006	mg/l	0.06	mg/l
total PAH	Organic components	0.0003	µg/l	0.001	µg/l
total PCBs	Organic components	0.00003	µg/l	0.0001	µg/l
total THM	Organic components	1	µg/l	50	µg/l
benzene/ benzol	Organic components	0.2	µg/l	1	µg/l
total pesticides	Pesticides	0.003	µg/l	0.01	µg/l
diclofenac	Pharmaceuticals	1	ng/L	5	ng/l
naproxen	Pharmaceuticals	1	ng/l	7	ng/l
ethynil-estradiol	Pharmaceuticals	0.001	ng/l	0.01	ng/l
Hexabromocyclododecane	Flame retardant	0.05	ng/l	0.2	ng/l
Coliform	Microbiology		CFU/100 ml		CFU/100 ml
Escherichia coli	Microbiology		CFU/100 ml		CFU/100 ml
Enteroccus	Microbiology		CFU/100 ml		CFU/100 ml
colony count 22°C	Microbiology		CFU/ml		CFU/ml

The sampling frequencies associated with the components defined in the sampling plan will vary from site to site. In the case of surface waters, many components are analysed monthly

(chemical and biological parameters, organic contaminants, drug residues) and the frequency of metals and pesticides determined in the other component groups varies. Metals are tested quarterly, while pesticides are also tested four times a year, but at different times. The definition of pesticides is scheduled for the spring months, as their releases to the environment are significant during this period. Due to the significant agricultural activity on the Hungarian side, the environmental exposure is higher in these months. As a result, we considered it justified to use shifted sampling to monitor surface and groundwater as well, in order to get a realistic picture of the possible spread and maximum detection of pesticide contamination. Bottornya is somewhat outside from the examined section, so sampling is done on the spot with less frequency. At Letenye the effluent arrives directly into the Mura River via a pressure pipe, so at this sampling point two sampling points are determined on the Mura River.

3. Physical and chemical parameters

3.1. Water temperature

The temperature of the water in the rivers is determined by the air temperature, which is influenced by the turbulence of the water movements. Since the water of the smaller watercourses mostly originates from underground waters with an equalized temperature, their temperature changes are also more moderate. The water temperature of the larger rivers, on the other hand, follows the local mean air temperature. As a result of persistently low air temperature, the temperature of the water decreases, as a result of which the content of dissolved oxygen in the water is expected to increase, the biological activity decreases, thus the content of organic matter decreases and vice versa. Ice formation is the result of the water surface cooling below 0 °C, but freezing is only caused by the jamming of ice floes floating on the water surface.

In the examined section, the surface water temperature changed according to the season, while the temperature of the underground water was roughly balanced during the one-year period.
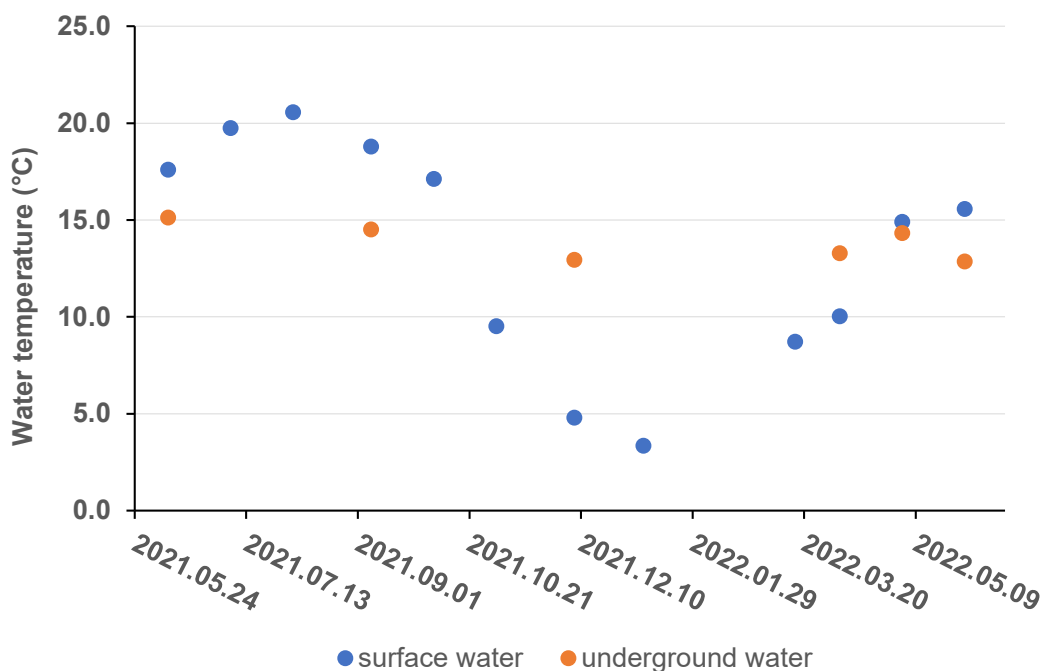
The change of water temperature during the investigated period

3.2. Dissolved oxygen, BOD, COD and TOC

3.2.1. Dissolved oxygen

The dissolved oxygen content of the water sample is determined with an electroanalytical dissolved oxygen meter. Results can be expressed as concentration (mg/l) or percent saturation (%). In practice, every liquid contains all the dissolved oxygen. Each liquid absorbs as much oxygen as the partial pressure of the oxygen in the liquid equilibrates with the air or gas phase in contact with it. The actual oxygen concentration thus depends on a number of factors, e.g., temperature, air pressure, the use of oxygen in microbiological degradation processes and from the oxygen production of the algae, etc., so it is a problem that the dissolved oxygen concentration of the water sample may change during transport, so in the case of natural waters, the measurement must be performed at the sampling site. The actual dissolved oxygen content of water, the quality of water, is best characterized by not giving its concentration but its amount expressed as a percentage of saturation. The value of oxygen content given in this way characterizes the biochemical state of the water in relation to total (100%) saturation; the discrepancy shows whether oxygen-consuming or oxygen-producing organisms are present in the water. The figure shows the dissolved oxygen content.
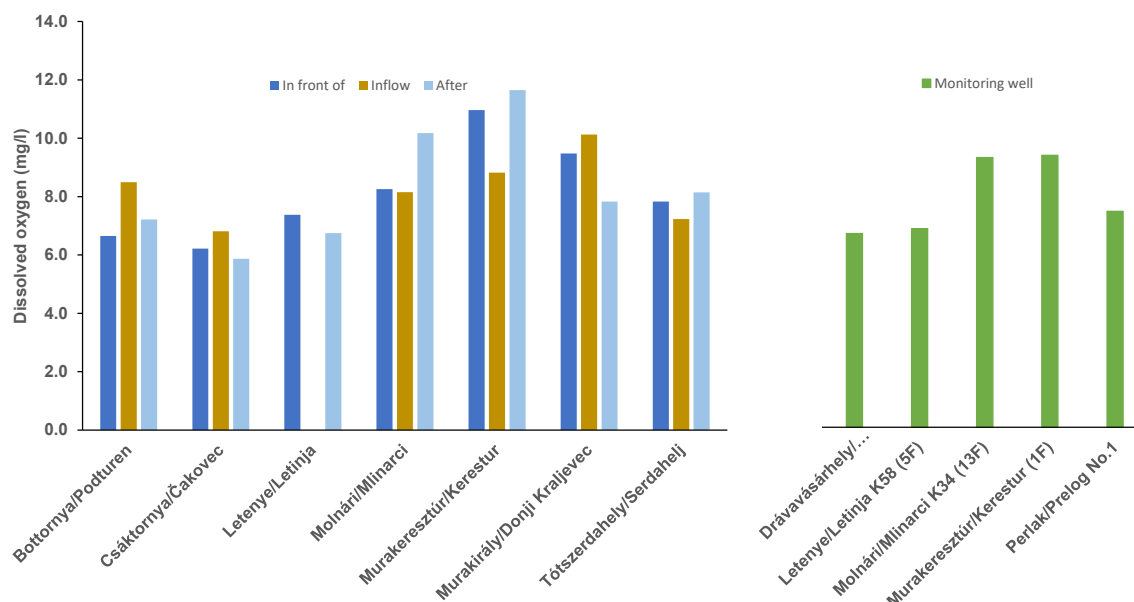
The change of dissolved oxygen during the investigated period

Oxygen conditions are considered to the most important status characteristic of living waters and are closely related to organic matter content. Oxygen is not only necessary for the respiration of aquatic organisms, but also for the heterotrophic bacteria use the dissolved oxygen content of water to break down organic matter. During the sampling period, the dissolved oxygen values measured in a given river section showed adequate levels.

3.2.2. Biological oxygen demand

Biological oxygen demand is an important parameter in water quality. The biological oxygen demand is the amount of dissolved oxygen required for the decomposition of organic matter in water by aerobic bacteria over a period of time and temperature. Based on the value of the biochemical oxygen demand, we can deduce the extent of the organic matter content of the tested sample. The BOD is given in mg/l of oxygen and is used to express water ("strength") contamination. The measured BOI_5 values are shown in the figure.
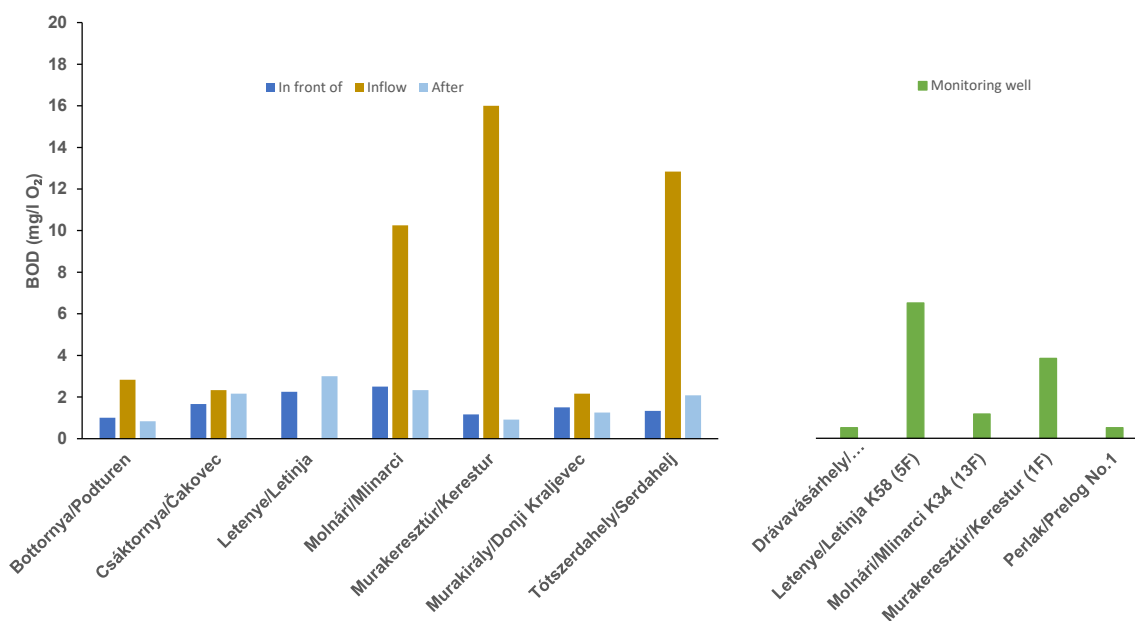
The change of BOD during the investigated period

Biological oxygen demand provides quantitative information on a fraction of the organic matter content, the amount that can be biodegraded. The measured values show higher values after the sampling points downstream of the sewage treatment plants, which is related to the incoming wastewater load.

The measured values from the Mura River do not show significant changes after the intake points and can therefore be concluded not to be significantly affected. The legal limit for surface water is not exceeded at any of the sampling points.

3.2.3. Chemical oxygen demand

The amount of organic pollutant in the water can be approximated by the chemical oxygen demand (COD, mg/l). The determination of COD thus gives the amount of oxygen required for the chemical oxidation of organic matter in water. It is based on the fact that all organic compounds, with few exceptions, can be oxidized to carbon dioxide and water with a strong oxidizing agent. In the COD determination, all organic matter is oxidized to carbon dioxide and water, regardless of whether the organic matter is biodegradable or not.
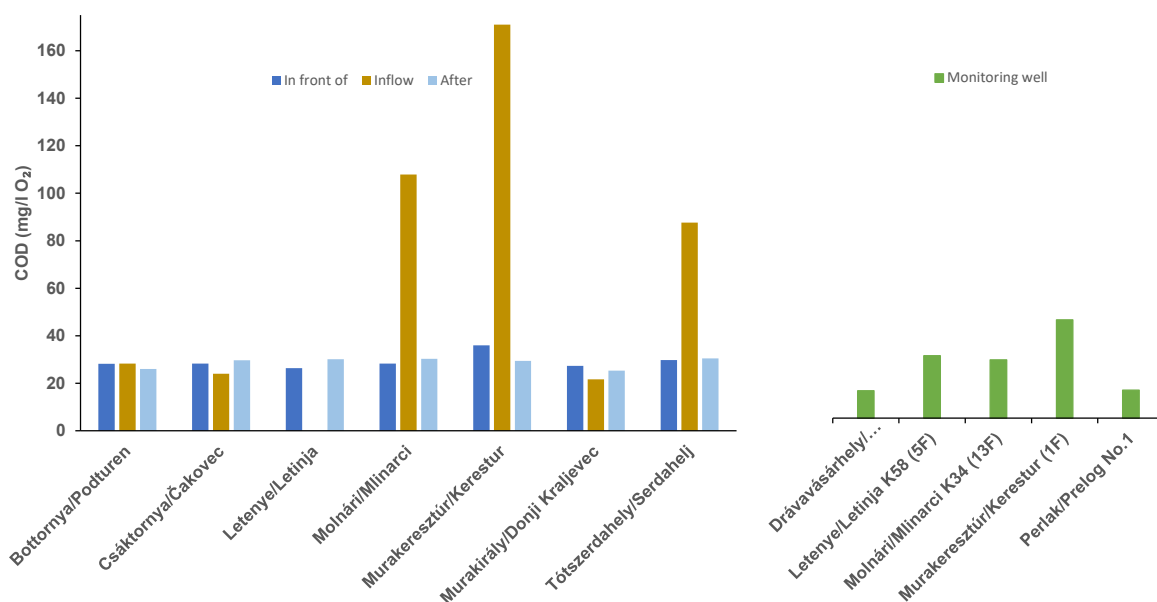
The change of COD during the investigated period

The chemical oxygen demand (COD) can be determined more accurately in practice, in which case oxidation is carried out chemically with an oxidising agent. There are strict regulations on chemical oxygen demand discharges, which must be followed for release to surface water. The data show that the COD of water discharged at three sites is quite high, but this value decreases rapidly as it is diluted. These values can be caused by inadequate treatment of wastewater or abnormal operations of wastewater treatment plants, perhaps in some cases the chlorine content of the samples was high at the time of the measurements, which affected the results. These high

discharges can be most dangerous in drier periods when higher concentrations remain after discharge into the river.

3.2.4. Total organic carbon

The total organic carbon content also refers to the amount of organic matter in the waters. The parameter (TOC) is more and more widespread in water analysis today than the chemical (COD), and as biological oxygen demand (BOD). TOC instrumentation is more reliable, sample "manually" defined BODs and generally BOD values are lower than TOC values. Also, it is becoming more common to determine the total organic carbon content of waters instead of chemical oxygen demand as a method of determining organic matter, because the disadvantages of methods used to determine COD are that reducing inorganic substances in water react with potassium permanganate or potassium dichromate can be done with a positive error.
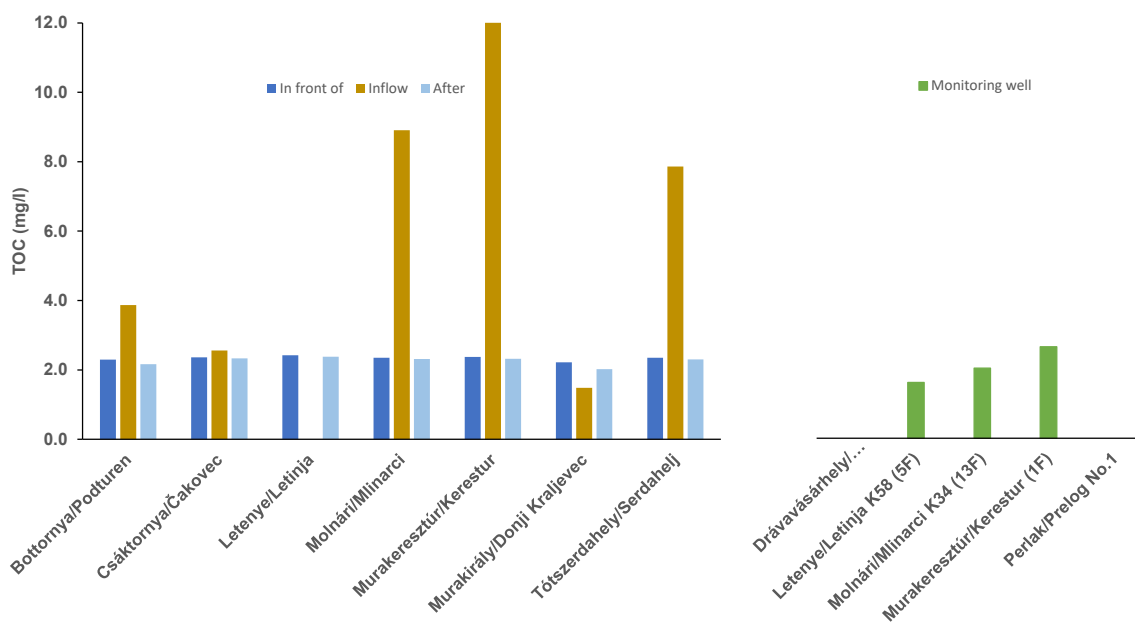
The change of TOC during the investigated period

The TOC results show a high value for three locations, which are normalised at the points after the inflows. This could be caused by organic matter enriched at the measurement points and diluted to the post-inflow measurement points. In most cases parallels can be drawn between TOC and COD results, in this case this can be fully said.

3.3. Turbidity, conductivity and pH

Turbidity is the measure of relative clarity of a liquid. It is an optical characteristic of water and is a measurement of the amount of light that is scattered by material in the water when a light is shined through the water sample. The higher the intensity of scattered light, the higher the turbidity. Material that causes water to be turbid include clay, silt, very tiny inorganic and organic matter, algae, dissolved coloured organic compounds, and plankton and other microscopic organisms. High concentrations of particulate matter affect light penetration and ecological productivity, recreational values, and habitat quality, and cause lakes to fill in faster. In streams, increased sedimentation and siltation can occur, which can result in harm to habitat areas for fish and other aquatic life. Particles also provide attachment places for other pollutants, notably metals and bacteria. For this reason, turbidity readings can be used as an indicator of potential pollution in a water body (https://www.usgs.gov/special-topics/water-science-school/science/turbidity-and-water).
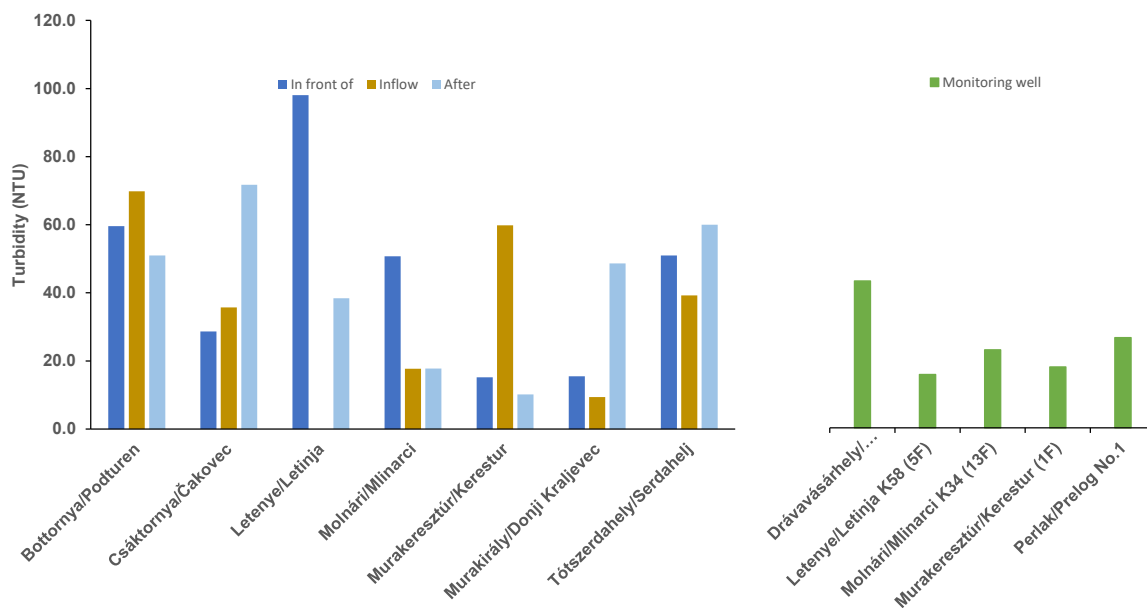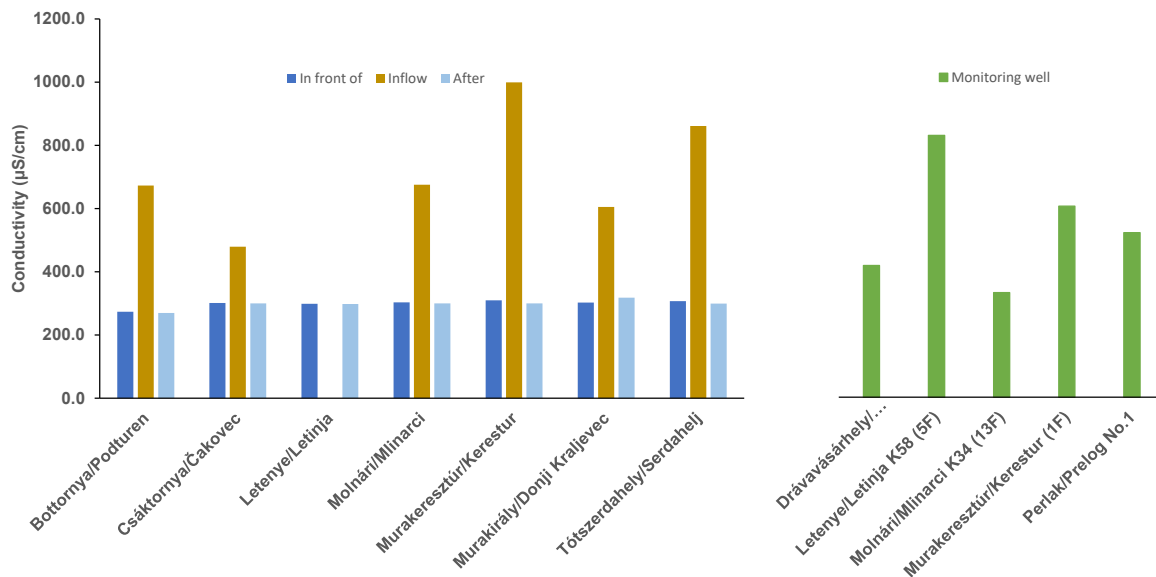

The change of turbidity during the investigated period

In the case of turbidity, no correlation can be established between the values of the water of the river and the tributaries. The measured values ranged from 0 to 40 NTU. Extreme values were not observed in any of the sampling locations.

Conductivity measures how easily electricity flows through water. Just like metal, water can conduct (transport) electricity. This is because there are salts dissolved in the water. If you have

pure water with no salts, conductivity will be zero. Conductivity often fluctuates seasonally. As water gets warmer, conductivity goes up. Additionally, if lakes do not receive enough rain or stream water, conductivity increases. This is because evaporation takes water away but does not take salts away. When ice forms on a lake in winter, the water below may also become saltier because salts are not incorporated into the ice. When the snow and ice melts in the spring, conductivity usually goes down because the meltwater dilutes the concentration of salts. Each lake and stream tends to have a relatively constant range of conductivity. This can be valuable information to have as a baseline for comparison. Significant changes in conductivity outside normal seasonal ranges could indicate a source of pollution (https://datastream.org/en/guide/conductivity).

The change of conductivity during the investigated period

In the case of conductivity, it can be established that the values measured at the sewage inlets on the Mura River were higher than in the river water, which is due to the ionic content of the treated sewage. The values of the underground waters were also higher than those of the river, the reason of which lies in the higher mineral content of the well waters. Overall, it can be concluded from the measured values that exceptionally high data was not experienced.

The pH of river water is the measure of how acidic or basic the water is on a scale of 0-14. It is a measure of hydrogen ion concentration. Natural water falls between 6.5 and 8.5 on this scale with 7.0 being neutral. The optimum pH for river water is around 7.4. Water's acidity can be

increased by acid rain but is kept in check by the buffer limestone. Extremes in pH can make a river inhospitable to life. Low pH is especially harmful to immature fish and insects. Acidic water also speeds the leaching of heavy metals harmful to fish (https://www.grc.nasa.gov/www/k-12/fenlewis/Waterquality.html).
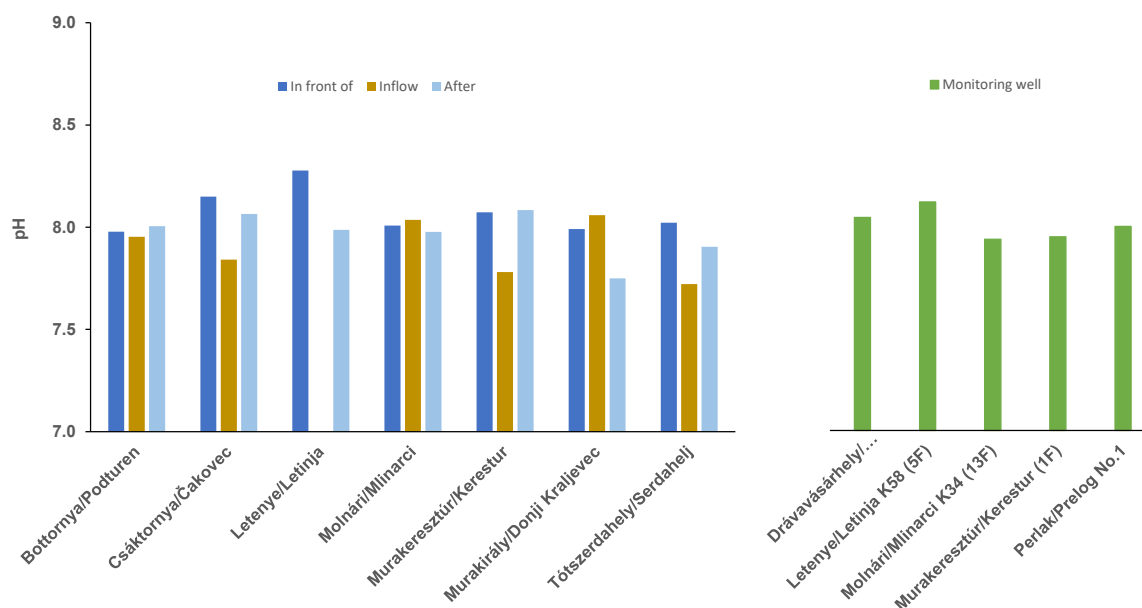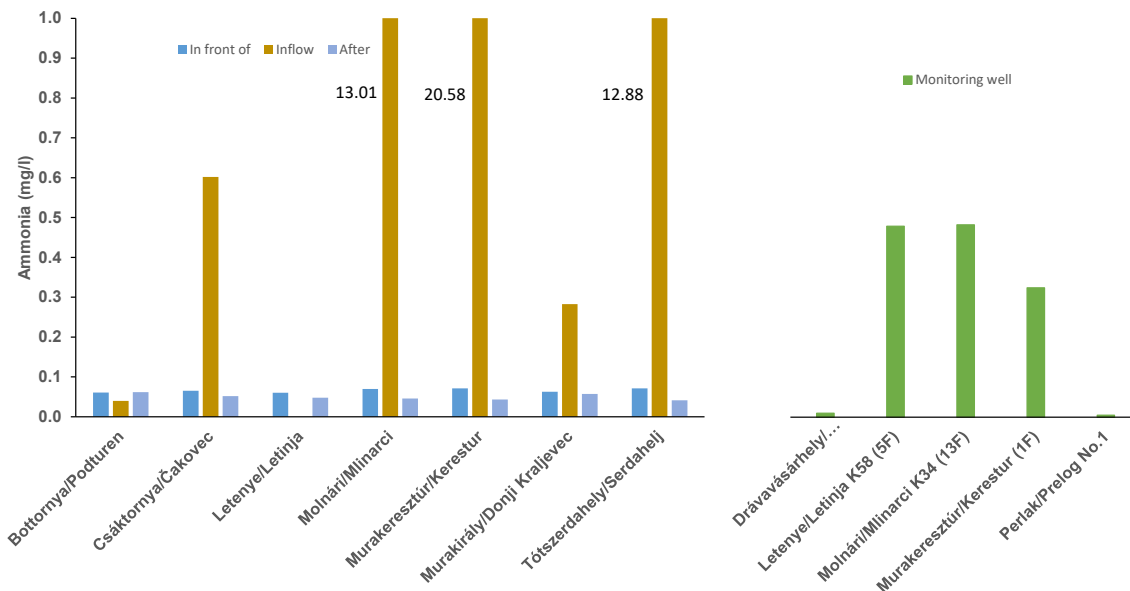

The change of pH during the investigated period

In the case of the pH values, it can be determined that they varied between 7.5 and 8.5, which fall into the slightly alkaline range.

3.4.   Nitrogen and phosphorus

Ammonium (NH_4^+) is required to know the amount of different forms of nitrogen in the study of water metabolism, in the determination of different self-purification processes, and in the characterization of water quality in general. Of the nitrogen forms, ammonium is what appears as a dissolved gas in water. Ammonium pollution is an indicator of water quality: organic matter, decomposed during the life of microorganisms and formed as a product of this. It may result from the leaching of municipal and industrial wastewater in surface waters and therefore indicates contamination of the waters.

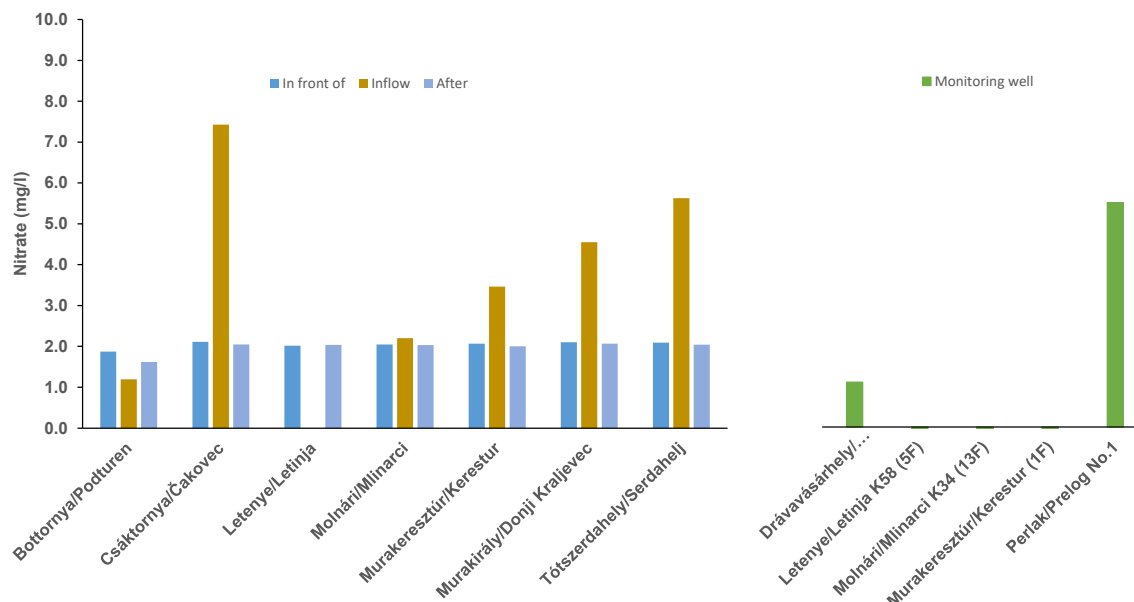*The change of ammonium during the investigated period*

The data clearly show that ammonium concentrations are extremely high at three of the inflow points (higher than the axis) and then fall rapidly once the ammonium is discharged into the river. The data after the inflow points are lower than those before, which may be explained by the fact that the nutrients that were released were degraded by aquatic organisms or otherwise bound in the water. For the three values above 10 mg/l (Molnári/Mlinarci, Murakeresztúr/Kerestur, Tótszerdahely/Serdahelj), the biological treatment of the wastewater treatment plants may not be operating properly, as confirmed by the nitrite/nitrate data examined in the next section. Based on the present study, the higher ammonium concentrations in the inflow did not have a serious impact on the river, but in the longer term and during drier periods they may cause eutrophication, which could seriously damage aquatic life. Ammonium is toxic, so its transformation into nitrate is important.

Nitrate is essential for plant development, but it can also cause environmental problems. Pollution indicating water quality parameters: e.g. excessive use of fertilizer dissolves from the soil into the water. In surface waters, nitrate ion is usually present in low concentrations, as ii the case of Mura River, as illustrated in the figure. Furthermore, the nitrate content also provides information on the self-cleaning processes of surface waters.
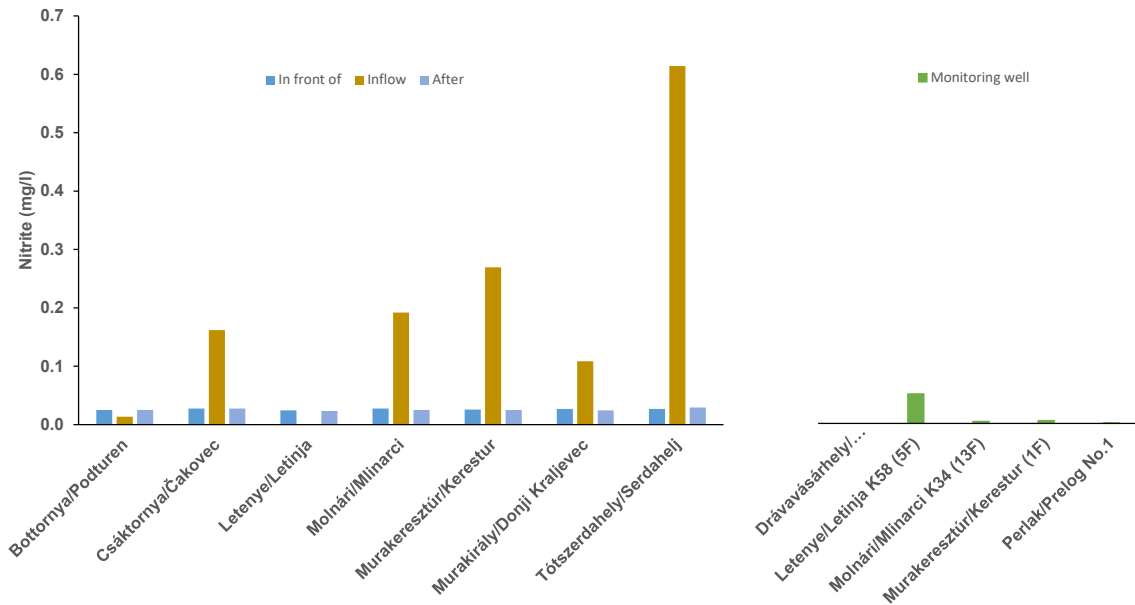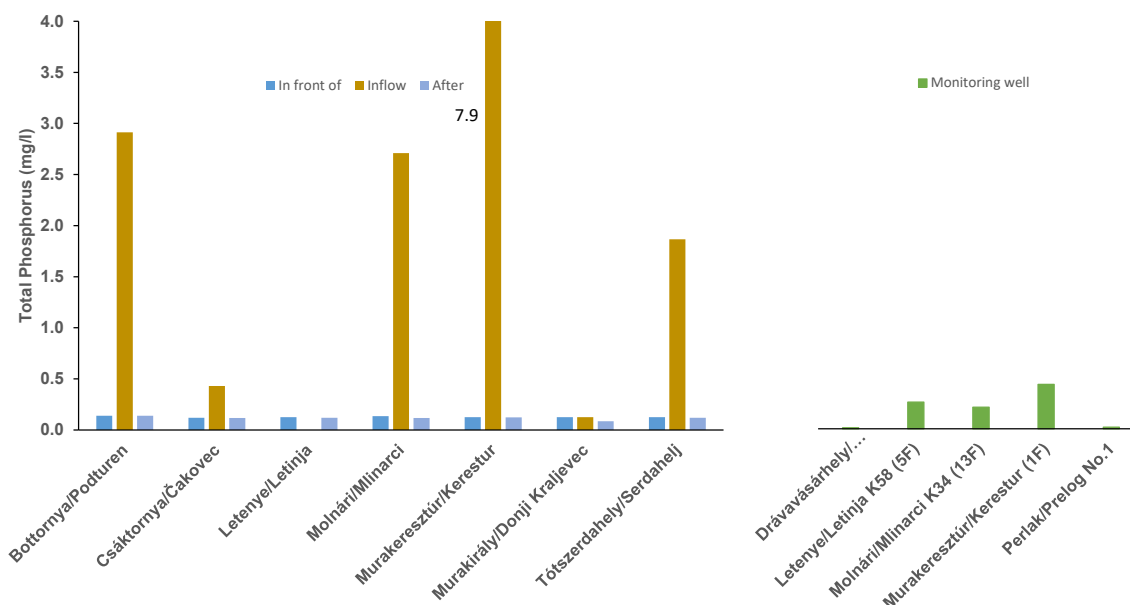

The change of nitrite during the investigated period

The first compound formed during nitrification is nitrite, which is formed from ammonium and further converted to nitrate. Its conversion to nitrate is important because nitrite (like ammonium) is toxic. With proper treatment, the concentration of nitrite should be lower than that of nitrate, as it is an intermediate product that is rapidly degraded by the micro-organisms. The diagrams show that nitrification is worst at the three inflow points mentioned above, where nitrite is higher than nitrate. This further proves that the treatment of wastewater here is inadequate, which may be caused by the possible short retention time of the biological treatment, as these microorganisms need the most time for the degradation processes. It can also be caused by high ammonium concentration entering the treatment plant, or by an inadequate environment such as a poorly adjusted pH or low dissolved oxygen. The data also show that higher concentrations are well diluted after discharge into the river in this case.

The change of nitrate during the investigated period

Phosphorus is a building block of living things. Unlike other elements, it occurs in the body in a higher proportion than in the environment. It is present almost exclusively in the fully oxidized form in the biosphere, most commonly as phosphate (PO_4^{3-}). Agricultural activities (organic fertilization, fertilization, livestock farms) and municipal wastewater discharges are responsible for the highest levels of phosphate entering water. Based on the measured data, the water quality meets EU requirements.

The change of phosphorus during the investigated period

Phosphorus concentrations are also closely related to nitrification and other degradation processes. In wastewater treatment, its amount can be a limiting factor in ammonium degradation, and it can provide a significant nutrient load when released into the environment (Nowak et al., 1996). The diagram shows that four inflow points had particularly high concentrations. In the case of Bottornya/Podturen, this can be explained by the fact that the degradation processes do not require high phosphorus (low initial ammonium) and therefore the influent nitrate concentration was low. Molnári/Mlinarci, Murakeresztúr/Kerestur, Tótszerdahely/Serdahelj, however, provide further evidence of abnormal functioning of the treatment plants, as the phosphorus content of the treated effluent is significant, so the amount needed for biological treatment is certainly sufficient. The higher concentrations discharged into the river are rapidly diluted, but in drier periods, they can cause problems of enrichment, leading to eutrophication.

3.5. Removal of nitrogen and phosphorus

Activated sludge for the biological treatment of residential wastewater was developed in the first decades of the last century, until the middle of the century it was designed only to remove organic oxygen, which causes the oxygen overload of the recipients. However, the treated effluent from such plants to the recipients is now a worldwide concern. The amount of nitrogen and phosphorus that are not absorbed by microorganisms can upset their ecological balance by entering natural recipients and living waters. This is a common phenomenon today in lakes, slow-flowing water bodies, reservoirs, and even shallow coastal waters. Excessive loading of inorganic (N and P) nutrients relative to organic matter in residential wastewater has in many cases led to severe eutrophication of recipients. This may have resulted in the overgrowth and algal blooms of plant organisms and algae. The consequences are known: the formation of floating foam on the surface of the water, the formation of sticky sludge in the water in bathing areas, the production of toxins by cyanobacteria, which then cause skin irritation and respiratory failure, problems in the population and in aquatic animals.

The use of nocturnal oxygen by algae and the bacteria that utilize them can cause severe oxygen deficiency during the period, which can lead to severe algae and sludge decay, and the development of hydrogen sulfide if nitrate is depleted from the water in addition to oxygen. Under these conditions, toxic nitrite may be formed, or the previously bound phosphorus may be redissolved in the cellular material of the dying microorganisms and algae, as well as in the

bottom sludge. The production of drinking water is also significantly more difficult and costly from eutrophied, high algae living waters than from healthy natural waters. Accordingly, in addition to the removal of organic matter from wastewater, one of the most important tasks of modern wastewater treatment today is the much more efficient removal of inorganic nutrients, nitrogen and phosphorus (http://www.vitigroup.hu/letoltesek/1_3_foszfortartalom-eltavolitasa-a-szennyviztisztitasnal.pdf).

In natural waters, ionic forms of inorganic nitrogen (nitrate and ammonium) are not essential for the growth of cyanobacteria (blue-green algae), as they can also assimilate molecular nitrogen to build their cellular material. Through their photoautotrophic metabolism, algae utilize the inorganic carbon content of water (CO_2 dissociating into HCO_3^-) as a carbon source. It is therefore necessary that phosphate in living waters to be a key component in determining the growth of algae, the concentration of which is the so-called growth-limiting factor. Eutrophication can only be significantly reduced in phosphates below 10 mg/l phosphate (Dryden and Stern, 1968).

In contrast to nitrogen compounds (ammonium and nitrate), which can be removed from water in gaseous form by biological processes, phosphorus can only be removed from wastewater in solid form by sedimentation. This is possible by incorporating phosphorus into the biomass from organic matter, by immobilizing it, or by precipitating the phosphate with a chemical. In the case of traditionally operated wastewater treatment plants, where only the removal of organic matter, possibly the removal of excess ammonium and then nitrate is the goal, the average amount of 7-12 mg/l of phosphorus arriving with raw residential wastewater, only 30–40% can be removed by so-called primary sludge and secondary sludge from dissolved and fine suspended organic matter (Nesbitt, 1969; Jardin, 1995). In order to avoid a strong algae growth in the recipients and living waters, an efficiency of over 90% in the removal of phosphorus should be ensured (Schaak et al., 1985). This means that only 0.5-1.0 mg/l phosphorus would be allowed in the effluent of the wastewater treatment plant. In order to achieve such a low concentration (<1 mg/l) in purification, various chemical phosphorus precipitation methods have been developed.

However, it has been revealed for about three decades that, if properly operated, certain groups of microorganisms can be encouraged to take up and remove significantly more phosphorus. In order for such increased biological phosphorus removal to be provided by the activated sludge system, it is necessary to treat the sludge cyclically under aerobic and then anaerobic conditions. In the aerobic phase, properly developed microorganisms capable of removing excess phosphorus (so-called poly-P bacteria) can store high concentrations of phosphorus in the

intercellular stock in the form of polyphosphate (Levin and Shapiro, 1965; Yall et al., 1970; van Loosdrecht and et al., 1997). At the same time, microorganisms capable of absorbing excess phosphorus in the anaerobic phase or cycle (anaerobic environment) depolymerize the stored polyphosphate and release it into solution, storing organic nutrients in their cells with the energy obtained from it (http://www.vitigroup.hu/tudastar-foszfortartalom-eltavolitasa-a-szennyviztisztitasnal).

Nitrogen removal (denitrification) can be achieved by supplementing conventional biological purification by creating anoxic spaces installed in different locations (pre-, post-, simultaneous denitrification, can be alternated in small colonies). Lower (70%) efficiency can be achieved with pre-denitrification and higher (80-85%) efficiency with post-denitrification. Nitrogen removal should be combined with chemical and / or biological P removal in all cases, and many of its technologies are widespread in Hungary. As the extra cost of removing N is higher than removing P, it should only be used in justified cases (https://edu.epito.bme.hu/local/coursepublicity/mod/resource/view.php?id=10024).

4. Metals

Contamination of heavy metals in the aquatic environment has attracted global attention owing to its abundance, persistence and environmental toxicity. Both natural and anthropogenic activities are responsible for the abundant of heavy metals in the environment. However, anthropogenic activities can effortlessly generate heavy metals in sediment and water that pollute the aquatic environment. The increasing pollution by heavy metals have a significant adverse health effect for invertebrates, fish, and humans. The metal pollution of aquatic ecosystems is increasing due to the effects from urbanization and industrialization (Ali et al., 2016).

4.1.   Iron and manganese

The figure shows the annual average of iron concentrations at each sampling site. With the exception of five sampling locations, the values were below 700 µg/l. In the right part of the figure, the higher values are shown separately. Among these, the Molnári 1 (Vicsa creek) point is outstanding, where the iron concentration was extremely high.
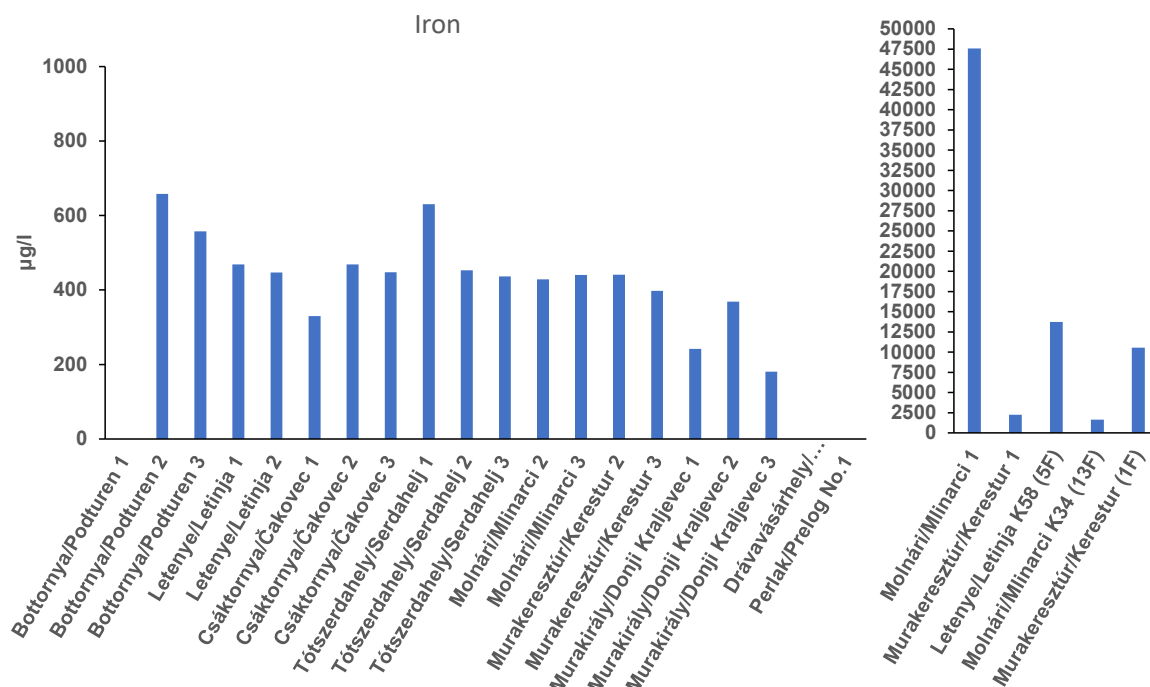
The change of iron concentration during the investigated period at each sampling point

The next figure shows the annual average of manganese concentrations at each sampling site. With the exception of four sampling locations, the values were below 150 µg/l. In the right part of the figure, the higher values are shown separately. Among these, the Molnári 1 (Vicsa creek) point is outstanding, where the manganese concentration was extremely high.
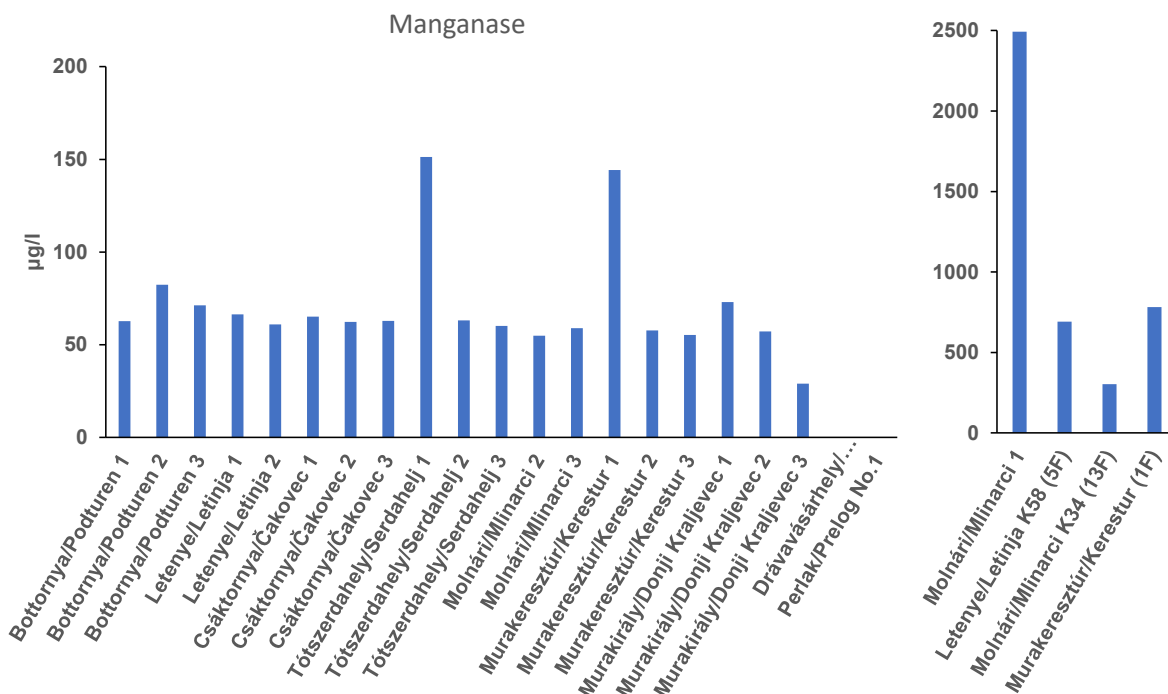
The change of manganese concentration during the investigated period at each sampling point

4.2. Removal of iron and manganese from drinking water

Consumption of iron and manganese is not harmful to the human body (it also needs iron), but for aesthetic reasons we need to remove these components from raw water.

Iron is present in groundwater under reductive conditions in a dissolved state. However, once on the surface, it oxidizes to a poorly soluble compound and appears as a brownish precipitate. According to the regulations of the previous (pre-2001) Hungarian Standard, the maximum permissible concentration is 0.2-0.3 mg/l, while according to the regulations of the European Union (and also valid in Hungary since 2001), the maximum permissible iron concentration is 0.2 mg/l in drinking water.

In order for iron to be removed from water by some solid / liquid phase separation technology, it must first be converted to a poorly water-soluble iron (III) compound.

The iron removal technology thus consists of the following basic processes:

- oxidation,
- chemical precipitation,

• solid-liquid phase separation.

The first step, the oxidation, requires the use of an oxidizing agent whose redox potential exceeds the redox potential of the iron (II) / iron (III) system.

The redox potential of the Fe^{2+} / Fe^{3+} system is + 0.77 V.

Redox potential of some oxidants:

   • oxygen dissolved in water (in neutral medium): +0.815 V,

   • oxygen dissolved in water (in acidic medium): +1.229 V,

   • ozone (in an alkaline medium): +2.07 V,

   • hypochlorous acid (in neutral-acidic medium): +1.49 V,

   • potassium permanganate ($KMnO_4$, acidic medium): +1.69 V,

   • potassium permanganate (alkaline medium): +1.85 V,

   • hydrogen peroxide: +2.14 V.

Thus, the oxidation of iron can be solved by using the above-mentioned chemicals. If only the iron needs to be oxidised (there are no other contaminants in the water that need to be removed that require oxidation), the use of air may be sufficient. In this case, the technology consists of a simple aeration followed by a solid-liquid phase separation (filtration and possibly pre-sedimentation). If other compounds (eg. arsenic, manganese) need to be oxidised in addition to iron, it is recommended to use a stronger oxidizing agent, such as chlorine, ozone, potassium permanganate.

The oxidation of iron (II) to iron (III) with each chemical takes place according to the following equations (Langlais, 1991):
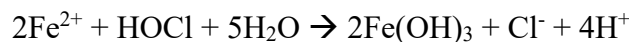
   • Oxidation of Fe (II) with oxygen (O_2):

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 5H2O \rightarrow 2Fe(OH)_3 + 4H^+$$

   • Oxidation of Fe (II) with ozone (O_3):

$$2Fe^{2+} + O_3 + 5H_2O \rightarrow 2Fe(OH)_3 + O_2 + 4H^+$$
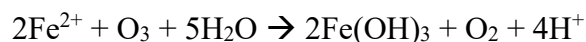
   • Oxidation of Fe (II) with hypochlorous acid (HOCl):

$$2Fe^{2+} + HOCl + 5H_2O \rightarrow 2Fe(OH)_3 + Cl^- + 4H^+$$

   • Oxidation of Fe (II) with chlorine dioxide (ClO_2):

$$Fe^{2+} + ClO_2 + 3H_2O \rightarrow Fe\,(OH)_3 + ClO_2^- + 3H^+$$

   • Oxidation of Fe (II) with potassium permanganate ($KMnO_4$):

$$3Fe^{2+} + MnO_4^- + 2H_2O \rightarrow 3Fe(OH)_3 + MnO_2 + 5H^+$$
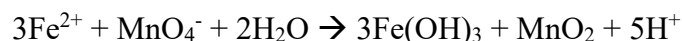
In case of manganese, according to the previous regulations of the Hungarian Standard (before 2001), the maximum permissible concentration was 0.05-0.1 mg/l, while according to the regulations of the European Union (and also valid in Hungary since 2001), the maximum permissible concentration in drinking water is 0.05 mg/l. The old Hungarian regulations

prescribed a combined concentration of iron and manganese of 0.3 mg/l. The European standard does not specify a specific limit for the combined value of iron and manganese.

Iron and manganese occurres in groundwater, protected aquifer and riverbank filtered water. Due to their reductive nature, water-soluble manganese (II) (Mn^{2+}) compounds dominate in these water bases. In order for manganese to be removed from water by some solid / liquid phase separation technology, it must first be converted to a poorly water-soluble manganese (IV) compound.

The manganese removal technology thus consists of the following basic processes:

- oxidation,
- chemical precipitation,
- solid-liquid phase separation.

The redox potential is + 1.51 V of the Mn^{2+} / Mn^{4+} system and + 1.28 V of the Mn^{2+} / MnO_2 system.

Thus, of the oxidizing agents listed above, air alone is not suitable for oxidizing manganese, it is necessary to use a stronger oxidizing agent (ozone, potassium permanganate). Based on the redox potential values, chlorine is in principle also suitable for the oxidation of manganese, but this is a very slow process.
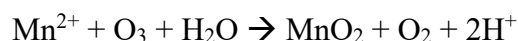
If the concentration of manganese in the water does not exceed 0.4-0.5 mg/l, the manganese present in the water can be oxidized using oxygen in the air without the use of a strong oxidizing agent. The essence of the process is to form a special catalytic layer on the surface of the filter particles. The catalyst layer can be formed by circulating a solution of $KMnO_4$ or $MnCl_2$ on filter sand. This forms a layer of MnO_2 on the surface of the filter particles, which can already be used as a catalyst to ensure that the manganese is oxidized by the oxygen in the air. The filter thus prepared is called an embedded filter. The application of the filter must be repeated at certain intervals (regeneration with $KMnO_4$ solution), since the catalyst only works if it is constantly renewed.

The oxidation of manganese (II) to manganese (IV) with each chemical takes place according to the following equations (Langlais, 1991):
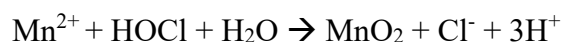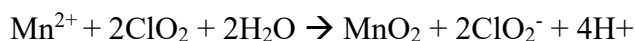
- Oxidation of Mn (II) with oxygen (O_2):

$$Mn^{2+} + \tfrac{1}{2}O_2 + H_2O \rightarrow MnO_2 + 2H^+$$
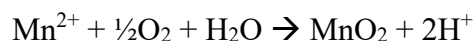
- Oxidation of Mn (II) with ozone (O_3):

$$Mn^{2+} + O_3 + H_2O \rightarrow MnO_2 + O_2 + 2H^+$$

- Oxidation of Mn (II) with hypochlorous acid (HOCl):

$$Mn^{2+} + HOCl + H_2O \rightarrow MnO_2 + Cl^- + 3H^+$$

- Oxidation of Mn (II) with chlorine dioxide (ClO_2):

$$Mn^{2+} + 2ClO_2 + 2H_2O \rightarrow MnO_2 + 2ClO_2^- + 4H+$$

• Oxidation of Mn (II) with potassium permanganate (KMnO₄):

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+$$

4.3. Cadmium, copper, lead

Cadmium is a member of the zinc group, but unlike zinc, it is very toxic. Cadmium accumulates in the kidneys and inhibits enzymes in the bone formation process. Causes osteoporosis and mucosal damage. It is only excreted from the human body in 10 years. Research has shown that cadmium inhibits their action by forming a stable complex with proteins.

The cadmium contents of the investigated area (all 25 points) were under 50 µg/l. Copper contents of the investigated samples were under 50 µg/l at all points, except for Molnári/Mlinarci 1 on 7th September, where it was a bit higher, but still under 150 µg/. Lead contents of the investigated samples were under 50 µg/l at all points, except for Molnári/Mlinarci 1 on 7th September, where it was a bit higher, but still under 150 µg/l.

## 4.4. Removal of cadmium, copper and lead

Researchers have developed and use a number of chemical and physical technologies to this day to successfully remove toxic heavy metals from wastewater. Such methods include precipitation, extraction with extractant, ion exchange, reverse osmosis, oxidation / reduction, sedimentation, filtration, various electrochemical methods, and the use of cationic surfactants. Wastewater containing copper, zinc, and cadmium is generated primarily during industrial or agricultural activities. The accumulation of heavy metals is a significant source of problems that requires the development of new wastewater treatment technologies. However, these conventional methods require further research and development due to their high operating costs, low removal efficiency and toxic sludge production side effects at low concentrations (http://www.hidrologia.hu/vandorgyules/36/word/0602_czikkely_marton.pdf).

4.5. Mercury

Like cadmium, mercury has no biological role, and its toxic effects are attributed, among other things, to its easy binding to thiol (-SH) groups and inhibition of basic biochemical reactions. Mercury is a neurotoxin in the body of fish and aquatic mammals, so it can get into the human body as well. The physiological effects of mercury have also been discovered by the Japanese in the wake of the pollution in Minamata Bay. Mercury has been introduced into the bodies of

people living around the bay with raw fish and shellfish, causing severe organ damage, musculoskeletal problems, blindness and brain cell death.

The figure shows the annual averages of mercury concentrations for each sampling location. It can be concluded that the concentration of mercury was below 1.5 μg/l in surface and underground waters (with the exception of one: ~4 μg/l).
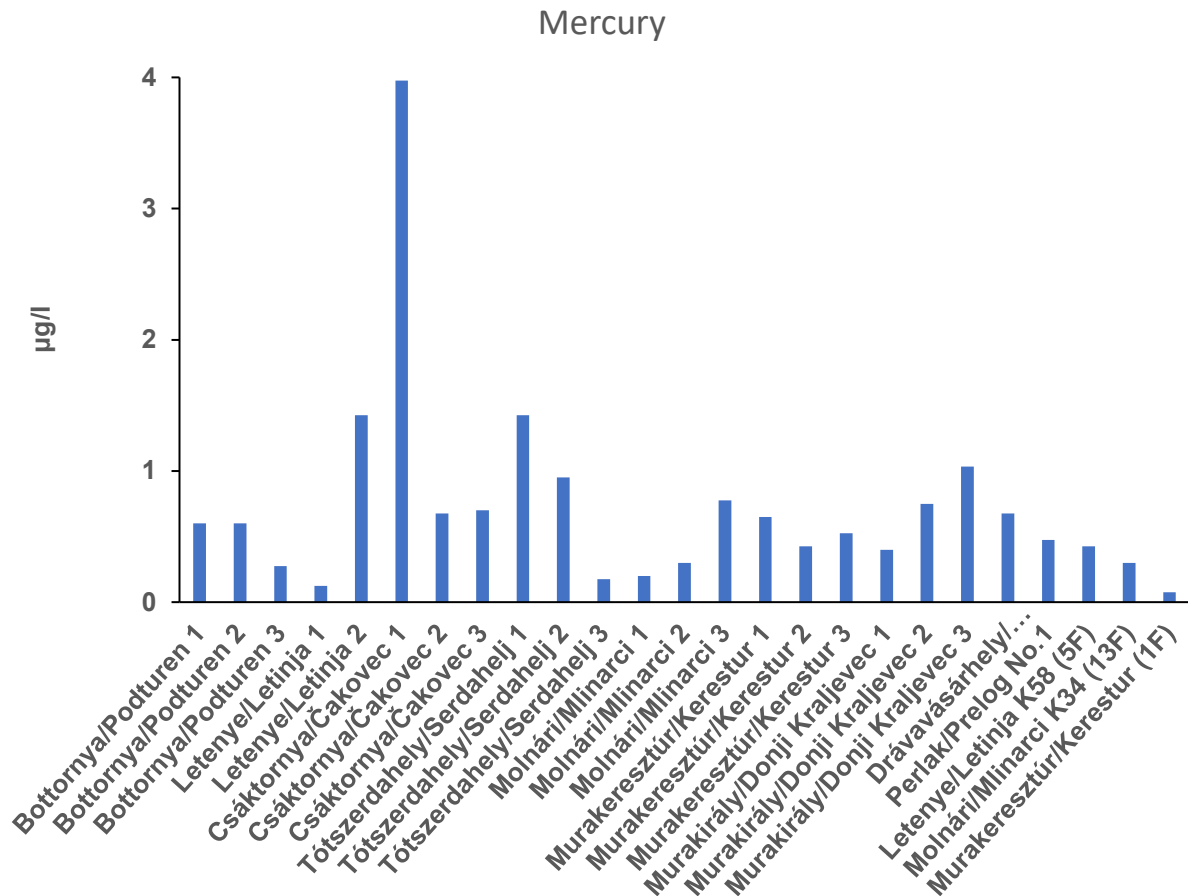
The change of mercury concentration during the investigated period at each sampling point

4.6.   Removal of mercury

Removing mercury from the water can be achieved using four processes: coagulation/filtration, granular activated carbon, lime softening and reverse osmosis.

Coagulation/filtration is a common treatment which uses $AlSO_4$ that reacts with the mercury to form a solid which can precipitate out of the water. The sludge then must be disposed of in a hazardous waste landfill. This process is beneficial because it costs very little and is reliable.

Granular activated carbon uses porous carbon media. This media is a very heavy charcoal material. As the water passes through, the dissolved contaminants are absorbed and held on the solid surface. This process has its limitations because the effectiveness depends on the concentration of mercury in the water.

Lime softening uses excess Ca(OH) to raise the pH level and then the heavy metal precipitates out as Hg(OH). A benefit of this method is lower costs and proven reliability.

In reverse osmosis, water is pushed through a semi permeable membrane. A common membrane material is a polyamide film. This produces high quality water, but is fairly expensive (https://people.uwec.edu/piercech/hg/mercury_water/removalmercury.htm).

4.7. Arsenic
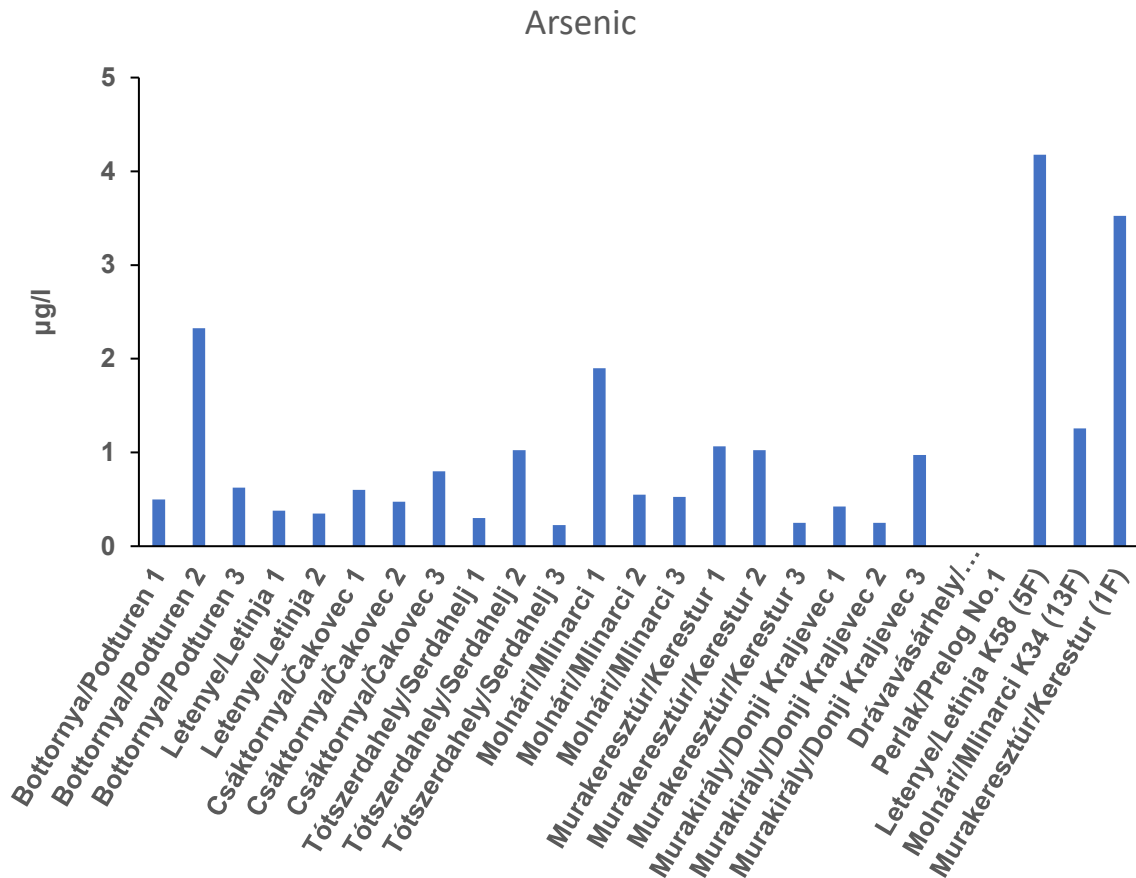
The change of arsenic concentration during the investigated period at each sampling point

The figure shows the annual averages of arsenic concentrations for each sampling location. It can be concluded that the concentration of arsenic in surface waters was below 3 μg/l. In the case of groundwater, it can be said that on the Hungarian side they were below 4 μg/l, while on the Croatian side it was almost undetectable.

4.8. Arsenic removal

In Hungary, water bases with high arsenic concentrations are subsurface, in which arsenic appears as a geological contaminant of natural origin. Arsenic is a proven carcinogen. When

inhaled, it causes lung cancer, and when it enters the body in other ways, it causes chronic cancer of the bladder, liver and skin (Csanády, 1998; Edwards, 1994).

One of the biggest challenges of joining the European Union in drinking water treatment is the problem of arsenic removal, as the maximum permissible concentration (50 µg/l) of arsenic in drinking water has been replaced. The new limit is 10 µg/l (according to the new regulations that came into force in October 2001). The tightening of the limit value approximately affects 1.3 million consumers in Hungary.

Arsenic is mostly present in water in inorganic form. Depending on the oxidative / reductive environment, arsenate [As (V)] and arsenite [As (III)] are present in the water. Arsenic exists in different forms depending on pH (Figure).
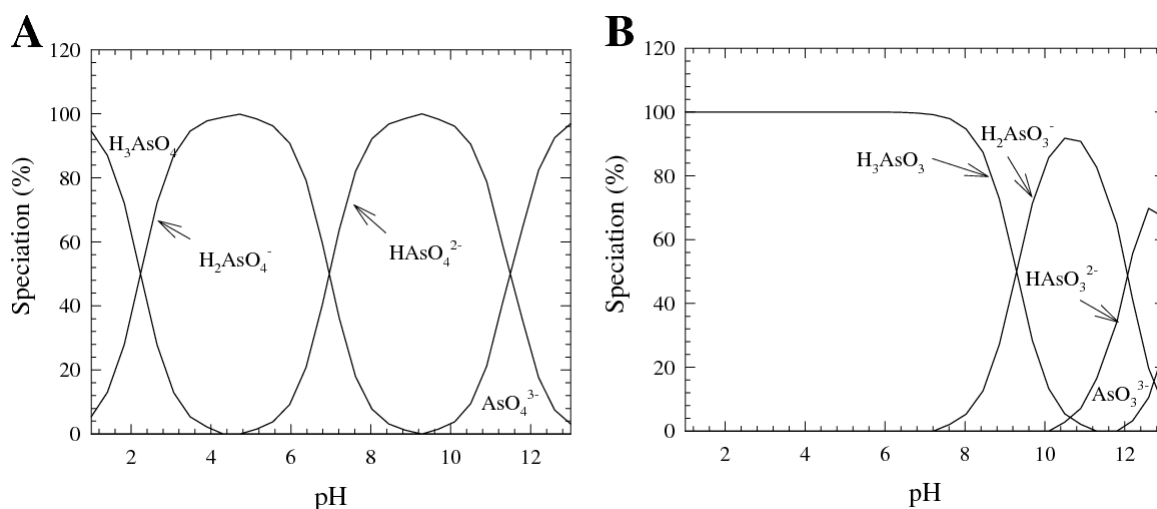
(A) arsenate and (B) arsenite speciation as a function of pH (Source: Weifang et al., 2007)

Occurrence of arsenate as a function of pH: H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}. Possible occurrences of arsenite as a function of pH: $H_4AsO_3^+$, H_3AsO_3, $HAsO_2$, $H_2AsO_3^-$, $HAsO_3$, AsO_3^{3-}. (Fields et al., 2000; DeMarco et al., 2003)

The figures show that at pH values around neutral, As (V) is mostly present in an anionic form in water ($H_2AsO_4^-$, $HAsO_4^{2-}$), while As (III) is mostly uncharged in the form of (H^3AsO^3). Because many water treatment technologies are capable of removing charged particles, while removing uncharged particles is a more complex task, this explains why the degree of oxidation of arsenic, preoxidation, plays such a significant role in the application of arsenic removal technologies.
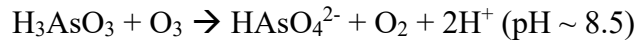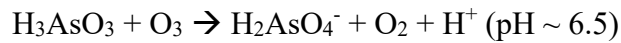
4.8.1. Removal of arsenic using coagulation / flocculation technology

The use of coagulation / flocculation technology significantly reduces the organic matter content of the water. Significant arsenic removal can also be achieved using this technology. In

deep waters, due to reductive conditions, some of the arsenic is present in reduced (As (III)) form. The first step in using coagulation / flocculation technology is to oxidize the reduced arsenic to arsenate (As (V)) for the reasons described above. The most commonly used oxidizing agents are chlorine, ozone, potassium permanganate.

The oxidation of arsenic takes place according to the following reaction equations:

• Oxidation of As (III) with ozone (O_3):

$$H_3AsO_3 + O_3 \rightarrow H_2AsO_4^- + O_2 + H^+ \text{ (pH} \sim 6.5)$$

$$H_3AsO_3 + O_3 \rightarrow HAsO_4^{2-} + O_2 + 2H^+ \text{ (pH} \sim 8.5)$$

• Oxidation of As (III) with chlorine (hypo: administered as NaOCl):

$$H_3AsO_3 + NaOCl \rightarrow H_2AsO_4^- + Na^+ + Cl^- + 2H^+$$

• Oxidation of As (III) with potassium permanganate ($KMnO_4$):

$$3H_3AsO_3 + 2MnO_4^- \rightarrow 3H_2AsO_4^- + 2MnO_2 + H_2O + 2H^+$$

The next step is to convert the oxidized but still dissolved arsenic to an insoluble form, which can be accomplished by coagulation-flocculation. A metal salt ($FeCl_3$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$) is added to the water with fast stirring followed by slow stirring to form flakes of the appropriate size. Arsenic precipitates with the resulting flakes / is incorporated into the flakes / adsorbed on the surface of the flakes. The conversion to solid form is thus the result of the following processes (https://archive.unu.edu/env/Arsenic/Han.pdf):

- precipitation: formation of insoluble $AlAsO_4$ and $FeAsO_4$, respectively,

- coprecipitation: incorporation of arsenic into aluminium and iron hydroxide flakes,

- adsorption: adsorption of arsenate [As (V)] molecules on the surface of iron and aluminium hydroxide flakes.

### 4.8.2. Removal of arsenic using adsorption processes

Arsenic can also be removed from water by adsorption processes. The adsorbent is charged to a column and the arsenic-containing water is passed through it. Arsenic binds to the surface of the adsorbent. The appearance and operation of filled columns is similar to simple sand filters. Adsorbents for arsenic removal:
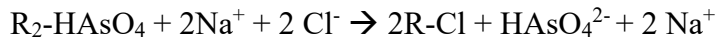
- activated alumina (Al_2O_3),
- granular iron oxide (eg. GEH filler),
- ion exchange resin to remove arsenic.

The alumina or iron oxide charges can be regenerated with NaOH solution, after which the adsorbent must be neutralized / rinsed with distilled water. In practice, however, the adsorbent is often replaced after the charge is depleted.

During ion exchange arsenic removal, Cl⁻ ions are introduced into the water instead of $HAsO_4^{2-}$ (R denotes the ion exchange resin):

$2R\text{-}Cl + HAsO_4^{2-} \rightarrow R_2\text{-}HAsO_4 + 2\,Cl^-$
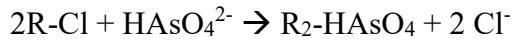
The charge is regenerated with NaCl solution:

$R_2\text{-}HAsO_4 + 2Na^+ + 2\,Cl^- \rightarrow 2R\text{-}Cl + HAsO_4^{2-} + 2\,Na^+$

In both the adsorption and ion exchange processes, the efficiency of adsorption can generally be increased by the use of oxidation.

4.8.3. Membrane technologies

Some membrane technologies (reverse osmosis) are suitable for the removal of dissolved contaminants, including dissolved arsenic. In this case, however, it is a problem that not only dissolved arsenic but also other dissolved components, including the mineral salts, are removed from the water, so it is necessary to re-salt the water after the membrane technology treatment. Another group of membrane technologies (where the pore size is larger, e.g., nanofiltration, microfiltration, ultrafiltration) can only partially be applied for this goal (e.g. nanofiltration) or it is necessary to apply a combined technology (e.g. lime softening and microfiltration). In this case, water pretreatment is required: oxidation, coagulation-flocculation is required, and membrane technology "only" plays a role as a solid / liquid phase separation technology.

5. Organic pollutants

Pollutants that are found in the environment in very low concentrations are called micropollutants. In the term micropollutants, the prefix "micro" indicates that they are present in amounts of only micrograms per liter, but in some cases they do not even reach a concentration of 1 ng/l. According to chemical grouping, organic and inorganic micropollutants are distinguished. Inorganic micropollutants can be heavy metals, arsenic, cyanides and their compounds. Organic micropollutants are biologically hard-to-degrade, often persistent, bioactive (affecting living cells and tissues) substances that occur in the environment at very low concentrations (less than a few μg/l) and have a potentially harmful effect on the environment and/or to living organisms. Organic micropollutants cannot be removed by conventional (traditional) wastewater treatment processes. Many of them do not or break down very slowly and can exert their harmful effects over a long period of time. These are called persistent organic pollutants (POPs), which have a half-life of more than a month, but often several years. Most of them are halogenated (mainly polychlorinated), substances that are less soluble in water and more soluble in fat, which promotes their accumulation in fatty tissues. Many of them are carcinogenic. In the case of non-persistent micropollutants, their rapid degradation/transformation is offset by their continuous replenishment. Due to the low concentration of organic micropollutants, they are generally not subject to environmental quality limits. Thanks to developing analytical methods, it is possible to detect more and more pollutants, so new and new substances are revealed to be found in the environment in very low concentrations and potentially harmful, these are called new pollutants (emerging pollutants – EP, emerging organic contaminants or contaminants of emerging concern – CEC). newly detected synthetic or naturally occurring pollutants, they are not subject to regulation and are not part of routine monitoring programs, there are no environmental quality limit values for them, but they are a cause for concern due to their potential harmful effects and/or persistent properties, and if there is sufficient evidence, environmental their occurrence will be regulated. The new pollutants did not necessarily enter the environment as a result of the environmentally damaging effects of recent years, often over a long period of time, they are constantly entering the surrounding waters and soil, but the analytics were not at such a level of development that they were able to detect pollutants found in low concentrations. In other cases, the synthesis of new chemical substances, or a change in the use or emission of existing ones, represents a new, potential threat to the environment. Thus, the category of new pollutants includes new, worrisome compounds from the point of view of environmental protection. The list of these substances is constantly changing, new substances appear, and as a result of the scientific results

of substances previously considered as new pollutants, their regulation takes place in the meantime, so they are no longer classified as new pollutants and are called traditional pollutants. In recent decades, as a result of legal regulations, the emission of pollutants regulated by environmental quality limit values has decreased significantly, as a result of which attention has been focused primarily on pollutants that are harder to detect and found in lower concentrations (Knisz et al 2020).

5.1. PCBs, THM and PAH

Trihalomethane (THM) compounds are primarily formed during the chlorination of drinking water, and accordingly, their most important source is the discharge of domestic and institutional wastewater. Volatile organic substances, their concentration decreases in the aeration systems of sewage treatment plants. Trihalomethanes are present in wastewater discharged directly from wastewater treatment plants that do not perform biological treatment or from sewer networks. THM emissions can be regulated by proper purification of drinking water.

Micro-pollutants can appear in water dissolved and/or in solid form. It is necessary to know what conditions in the given water space influence the distribution of individual components between the dissolved and solid state. The environmental conditions, the physical and chemical characteristics of the given water, as well as their changes, can fundamentally change the distribution of individual micro-pollutants between the dissolved and solid state. Organic suspended solids with a relatively low density and a high specific surface area have an excellent adsorption capacity for both organic and inorganic micropollutants. Inorganic suspended solids with a higher density but smaller specific surface area have a lower adsorption capacity, primarily the adsorption of organic components is inhibited. The adsorption capacity of suspended solids of mineral origin - especially for heavy metals - is greatly increased if the particle surface of the suspended solid has ion-exchange capabilities. Ion exchange adsorption significantly reduces the concentration of heavy metals in the dissolved state but increases those appearing in the solid state.

Xenobiotics (xenos = foreign; bios = life) are substances found in biological systems that are not produced in normally functioning biological systems. Every year, the chemical industry produces an increasing number and quantity of new active pharmaceutical ingredients, cleaning agents, paints, and cosmetic products, all of which belong to the family of xenobiotics. After use, these substances end up in municipal sewage treatment plants in unchanged form or as

metabolites, where the biodegradation of organic micropollutants does not or only partially takes place, so they can reach our drinking water bases after entering the receiving surface waters.

Regardless of their origin, the harmful effects of xenobiotics are determined by their quantity, frequency and biological activity. Our body gets rid of these substances through biotransformation, for which liver enzymes are responsible, and excretion with bile or urine.

Considering that due to climate change we have to account for the decreasing amount of rainwater and thus the increasing concentration of chemical residues, the increasing use of medicines due to the increasing average age and the expected increase in the standard of living, the use of detergents and cosmetics is of fundamental importance, the development of water purification technologies for water bases and in order to protect the ecological system.

Polycyclic aromatic hydrocarbons (PAH compounds) are extremely dangerous, and due to their limited water solubility, they mainly accumulate in surface water sediments. Currently, the source of PAH compounds in surface waters is primarily sediment. Polychlorinated biphenyls (PCB-derivatives) are included in the first half of the 20th century, it was widely used as a stabilizer for transformer oils and as a protective material for wooden materials against animal pests, but currently its use has decreased. Their solubility in water is limited, so they mainly appear in surface water sediments.

Phenols and phenol derivatives entered surface waters with industrial wastewater mainly during the period of intensive chemical processing of hard coal and lignite. Phenols and their derivatives do dissolve in water, but not well. Therefore, phenols released into surface water appear primarily in the sediment. However, during the stirring of the sediment, dissolved phenols from the pore water enter the water space, and as a result, their concentrations can sometimes reach a few µg/l (https://tudastar.mk.uni-pannon.hu/anyagok/26-Ivoviztisztitas.pdf).

During the survey, we did not experience any outliers or exaggerated values during the examination of these components. The maximum concentration of Total PCBs was 0.01 µg/l. Values around LOD were detected during THM measurements. Total PAH was detected between 0.004 and 0.266 µg/l.
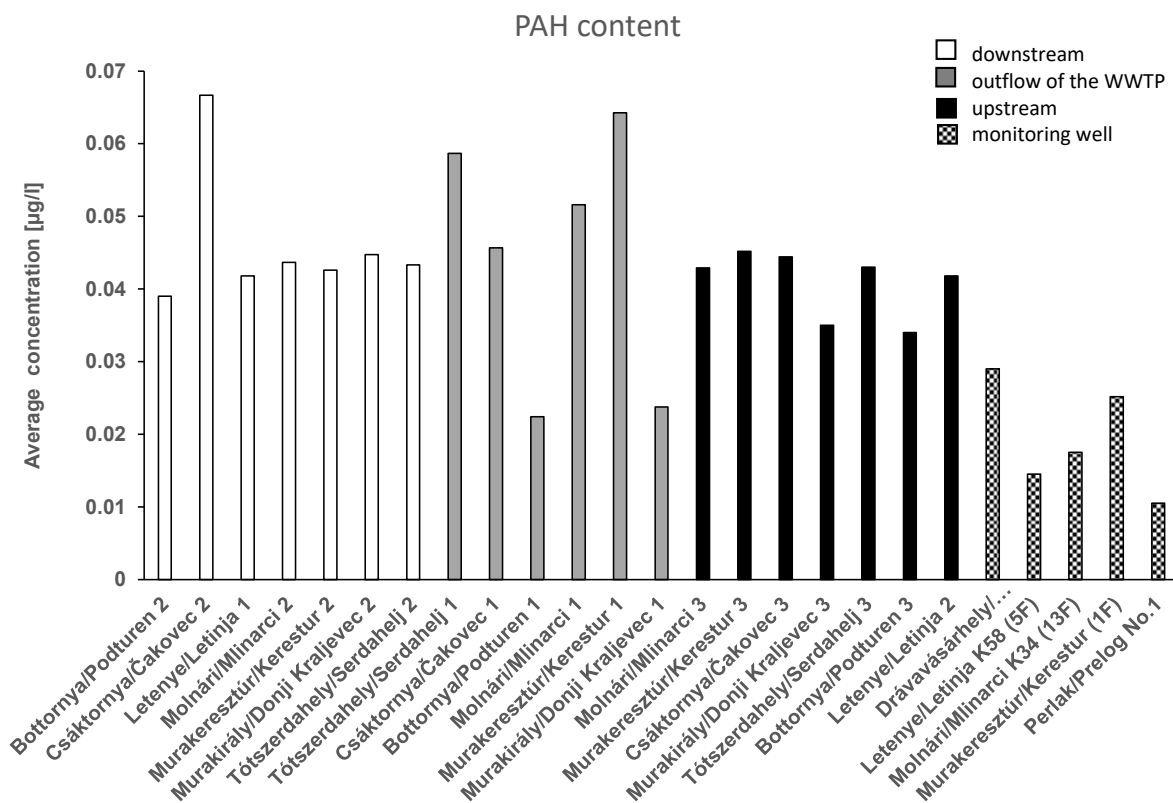
PAH content

The PAH content was presented in µg/l

The samples PAH content was similar despite the fact that the samples originated from different sample type (e.g. surface water, monitoring well).

5.2.   Pesticides

The protection of groundwater against pesticide pollution is a priority in global environmental policy, given that groundwater contamination can last for decades, cause significant damage to drinking water bases, affect the quality of groundwater, and pose a threat to the ecosystem of groundwater. The role of plant protection agents in suppressing bacteria, fungi and weeds that are harmful to agriculture is indisputable, therefore their use has increased significantly since the Second World War, both in terms of quantity and the number of types of agents. Pesticide pollution affecting groundwater bodies can be detected in all EU member states except Sweden. The primary way of getting into the environment is via diffuse pollution. The sources of diffuse pollution are difficult to define and typically affect large geographical areas. The main characteristics of these diffuse pollutants are:

a) the larger geographical dimensions;

b) it typically has a lower environmental burden than point sources;

c) the natural damping effect of the soil and subsoil is more likely to prevail;

d) it is difficult to limit and less clearly identify the emitter, which makes it extremely difficult to monitor and control diffuse pollution, as well as to determine what effect diffuse pollution may have on, for example, groundwater.

The most typical diffuse sources are agricultural areas, where a significant amount of pesticides, as well as sewage sludge and animal manure, which can be used to improve soil fertility, are spread.

Classic pesticides, most of which are contact nerve poisons (DDT, HCH) have a very stable structure, they do not decompose, and as a result they can remain unchanged in nature for hundreds of years. The use of these products in the 20th century was banned. Chlorinated hydrocarbon-type plant protection products have been replaced by substances that change their structure in a short time, i.e. decompose (e.g. phosphoric acid esters).

Pollution is particularly problematic in the Mediterranean region, where underground water resources can also decrease significantly during the dry season. It is important to emphasize the fact that groundwater bodies are usually not polluted by a single pesticide, but a mixture of different pollutants can be found in them. Despite the frequent occurrence of these pollutant mixtures, current EU regulations focus almost exclusively on the risk assessment of individual chemicals. However, the toxicity of pesticide mixtures is generally higher than the toxicity of individual components. This means that different compounds can contribute to the overall toxicity of a mixture even if they are individually present at low concentrations that do not cause adverse effects on freshwater life.

The herbicide glyphosate and its metabolite AMPA were the most frequently (FO 48 and 79) and the biggest amounts detected pesticide (7.5 and 20.6 µg/l) in this survey.
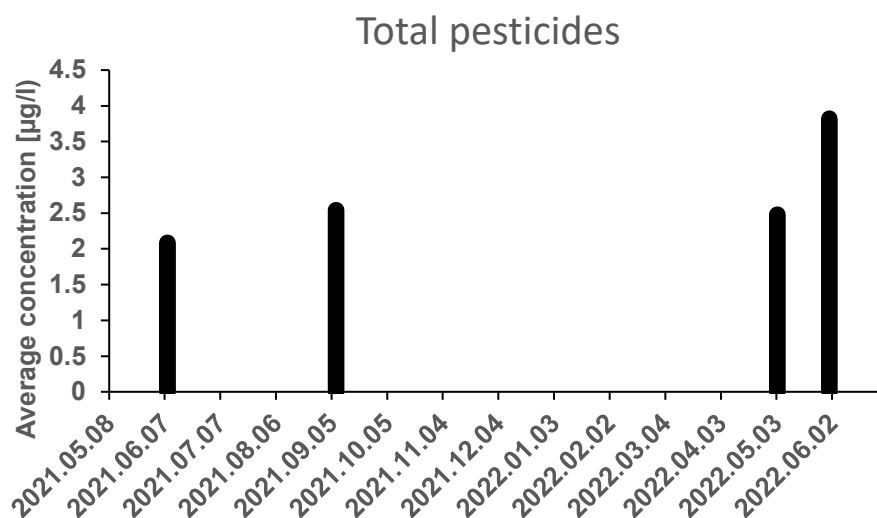
The figure represents the average concentration in µg/l of total pesticides.

Taking seasonal applications into account, we expected temporal variations in the case of pesticides. However, this was not observed in the case of total pesticides. In some cases in the observation wells were appaired some pesticides. These were the atrazine (0.01 µg/l at 2022.05.31 from Perlak and at 2022.05.03. from Drávavásárhely), desethylatrazine (0.01-0.04 µg/l from Perlak and Drávavásárhely), 2,4-D (0.04 µg/l from Perlak and 0.01µg/l from Letenye at 2022.05.31.) and bentazone (0.01 µg/l at 2021.06.28) from Murakeresztúr sampling point.

5.3.   Pharmaceuticals

Their main way of entering the environment is through point source pollution. This can be identified in a spatially well-defined way, the spatial extent of the pollution, i.e. the pollution plume, is spatially limited. We consider sewage plant effluents to be the most important point sources, although there are organic pollutants that do not enter the environment through sewage plant effluents. In addition to household waste, a significant amount of organic pollutants enter the environment through the sewage network. Collected or improperly destroyed medicines, cosmetics and personal care products, and other chemical agents can very likely end up in the sewage network. The traditionally used secondary treatment strategies, such as activated sludge and trickling-body systems, are not suitable for filtering most micropollutants, so they enter surface waters, rivers, lakes, and coastal waters with treated wastewater, and can wash into the soil with sewage sludge. The detection of some micropollutants in wastewater reflects its usage habits.

Compounds that disturb the hormone system, or the endocrine system as it is called, are one of the groups of greatest concern. According to the definition of the International Program on Chemical Safety (IPCS), an "endocrine disruptor is an exogenous compound or mixture that alters the function of the hormone system and, as a consequence, causes adverse health effects in the organism or its offspring or in the population (in a subpopulation)". While "a potential endocrine disruptor is an exogenous compound or mixture that has properties that are expected to lead to endocrine disruption in an intact organism or its offspring or population (subpopulation)".

Many hormonally active compounds can be detected in humans, wild animals, and environmental samples, some of which persist in the environment, while others degrade over time. Some of them are stored in the tissues, others are only present in the human body for a short time, but during a critical period of development. EDCs include natural hormones such as estrogens, androgens or plant-derived phytoestrogens, synthetic hormones (e.g. ethynil-estradiol), and any industrial compound or by-product that may disrupt hormone balance, such

as polycyclic aromatic hydrocarbons, polychlorinated biphenyls, dioxins, furans, alkylphenols, some PPCPs, pesticides or pharmaceuticals (e.g. diclofenac or naproxen).

Chemical pollutants, like PhACs, of surface water poses a threat to the aquatic environment, with effects such as acute and chronic toxicity in aquatic organisms, accumulation of pollutants in the ecosystem and loss of habitats and biodiversity, and also pose a threat to human health. According to the Environmental Quality Standards Directive (Directive 2008/105/EC) for determination of anthropogenic chemical pollutions at a global level, a new Watch List (WL) is needed to provide highquality monitoring information on the concentrations of polluting substances in the aquatic environment. The surface waterWL supports the identification of priority substances for regulation under the Water Framework Directive. The first WL was established in 2013 under the Directive 2008/105/EC (as amended by Directive 2013/39/EU), collecting four PhACs (E1, E2, EE2 and diclofenac). After, the WL was modified based on the Joint Research Center (JRC) Technical Report in 2015 (EU Commission JRC, 2015) and in April 2018 (EU Commission JRC, 2018), additionally, the latter provided several recommendations for the second WL. New candidate WL substances should be selected among substances posing a potential risk for the environment, but for which there is not enough good quality monitoring data to confirm this risk. Therefore, there is a continuing need for the development and optimisation of sensitive analytical techniques to detect and measure environmental substances (Maasz et al., 2019).

In this survey the most frequently detected pollutant was the NSAID diclofenac (FO 92%, av.: 246.2 ng/l). The estrogenic ethynil-estradiol was detected in more than half of the samples (FO 76%, av.: 0.33 ng/l). The NSAID naproxen was also detected at the same time (FO 42%, av.: 51.5 ng/l).
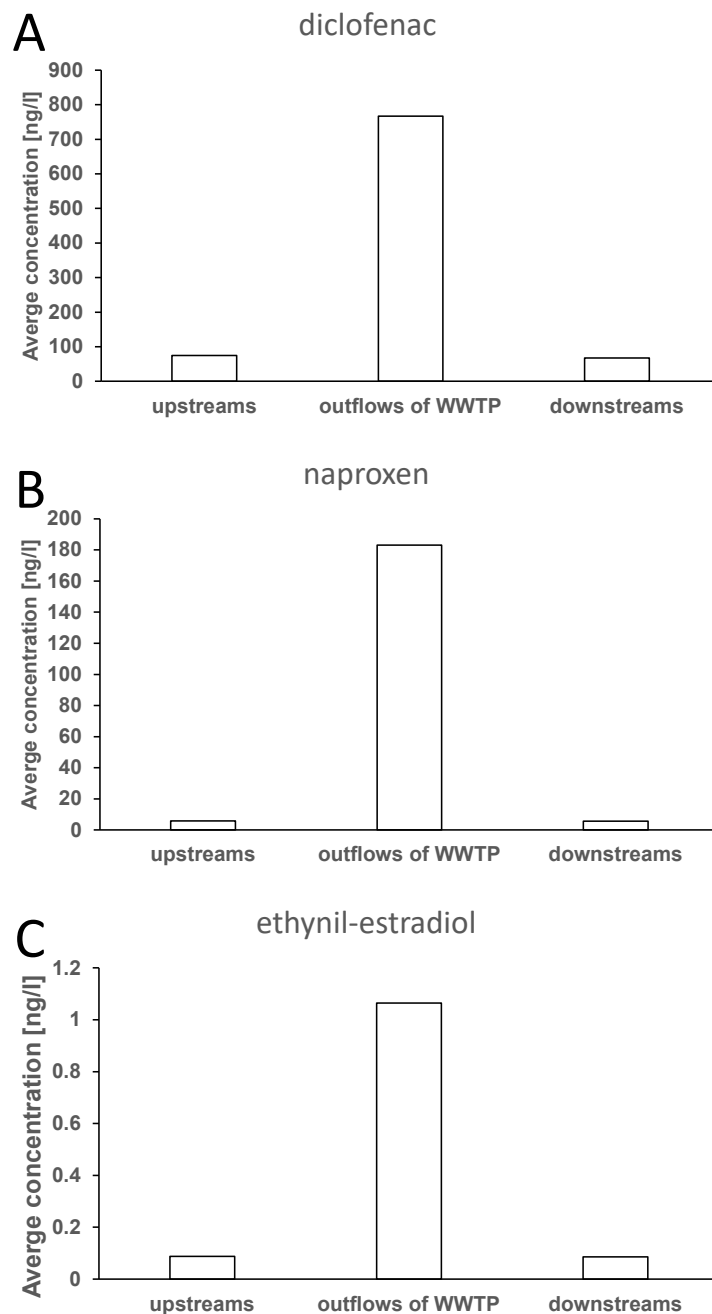
The average concentration in ng/l of diclofenac (A), naproxen (B) and the ethynyl-estradiol (C) on the upstreams of the Mura, the outflows of the WWTP and the downstreams of the Mura

It was found that WWTP effluents contain significant amounts of pharmaceuticals. The WWTP loads have a possible major role on the drug contamination of the studied area.

5.4. Removal of organic pollutants during wastewater treatment

The primary goal of wastewater treatment is to protect health, stop the pathogen cycle, and protect the ecosystem and host water bodies. The removal of substances subject to regulation, such as organic matter, plant nutrients, and pathogens, is usually achieved, and their concentration can be kept below the regulatory level in the sewage plant effluents, thereby relieving the recipient of the burden. However, organic micropollutants cannot be completely removed during wastewater treatment, so one of their most significant point sources is treated wastewater from wastewater treatment plants. In particular, so-called new pollutants are of concern, for which there are no limit values and which cannot be economically removed with traditional wastewater treatment methods. Most of the new pollutants that arrive at the sewage plant are also found in the treated sewage, as most of the municipal sewage treatment plants are not capable of removing them, one of the main reasons for this being that the pollutant remains in the effluent during the successive steps of the treatment process. Others are removed from the wastewater during cleaning, but often remain in the sludge, which is not completely broken down by traditional sludge treatment methods, such as composting and biogas production, so the use of nutrient-rich sludge as fertilizer in agriculture is an additional source of micropollution.

Municipal wastewater treatment basically takes place in three stages. In the first stage, mechanical cleaning takes place, the purpose of which is to remove coarse physical impurities, this is the so-called physical cleaning stage. This physical wastewater treatment stage is not suitable for removing micropollutants, especially hydrophilic pollutants. Hydrophobic micropollutants can strongly bind to the primary sludge from the pre-clarifier and can be partially removed from the dissolved phase during primary treatment.

In the second step, biological cleaning takes place, where wastewater treatment is carried out through microbial decomposition. The main goal is to remove organic matter and/or nutrients using biological processes (e.g. in aerobic or anaerobic systems). In this step, the micropollutants are either completely degraded (mineralization) or partially decomposed into transformation products.

The task of the third stage is to treat the residual components burdening surface waters, for example the removal of eutrophication-causing nutrients, various forms of nitrogen and phosphorus compounds.

In order to further protect the receivers, a fourth level of wastewater treatment and purification was formulated and introduced to deal with newly emerging anthropogenic pollutants and micropollutants (e.g. pesticides, drug residues, etc.), which aims to further remove these pollutants, as it has been confirmed that organic micropollutants are the they cannot be

completely removed during primary, secondary and tertiary cleaning phases. The quaternary stage can be chemical (e.g. precipitation, oxidation), physical (membrane filtration, activated carbon) or even biological (e.g. heavy metal binding with microalgae). In practice, three-stage systems were developed to remove these substances, but due to their cost and space requirements, they are only used in justified cases, at sensitive receivers (Tran et al 2018).

5.4.1. Physical Removal Processes

In the pre-mechanical part of wastewater treatment, the coarse grid removes (retains) pollutants larger than 10 mm, the fine grid removes those larger than 2-3 mm. The sand trap separates discrete particles larger than 0.1 mm, sand and grease, and then the pre-settler removes about 60% of the particulate matter (suspended matter – TSS). However, additional methods operating on the modern physical principle can also be integrated into traditional technology.

This can be, for example, activated carbon operating on the principle of adsorption, which can ensure the effective removal of most organic substances of low and medium molecular weight by adsorbing organic pollutants on its surface. It can be suitable for removing most persistent pollutants, the advantage is that it is affordable and can be provided in large quantities.

Another process that uses physical principles is filtration, which in practice is realized as membrane filtration. It is a separation process based on the semipermeable properties of membranes, allowing water to pass through and retaining dissolved or suspended matter depending on the type of membrane. There are four main types of membrane filtration: 1. microfiltration (MF), 2. ultrafiltration (UF), 3. nanofiltration (NF) and 4. reverse osmosis (RO). Although micro- and ultra-filters are effective in reducing turbidity, they are ineffective in removing organic micropollutants because the pore sizes are much larger than the molecular sizes of the pollutants. The size of organic micropollutants is typically below 500 Da, with a few exceptions (such as macrolide antibiotics), typically between 100 and 400 Da. On the other hand, the pore size of micro- and ultrafiltration membranes is between 10-500 thousand Da, that is, based on their size, they are unable to retain organic pollutants. In the case of NF and RO membranes, filtration based on size is already an effective removal method, NF membranes remove pollutants with a molecular size > 200 Da, while RO membranes remove pollutants with a molecular size of 100–150 Da. In addition to removal based on molecular size, two other removal mechanisms, charge-based removal and adsorption, also contribute to the removal of organic micropollutants. The polymers on the surface of the membrane bind organic micropollutants, so they can be removed during cleaning. It is important to emphasize that no

matter how effective the membranes are, the filtered organic micropollutants are only retained or concentrated, so their further treatment must be ensured.

Cyclodextrin-based materials are promising for the removal of organic micropollutants. Cyclodextrins are cyclic oligosaccharides consisting of six, seven or eight α-D-glucopyranose units. Thanks to their structure, they are able to increase solubility. Their outer surface is polar, so they dissolve in water. They are able to form so-called inclusion complexes, thereby increasing the water solubility of hydrophobic molecules. β-Cyclodextrin (β-CD) (the cyclic macromolecule of glucose, which consists of 7 glucopyranose units) is capable of binding organic micropollutants from water by absorption, however, due to its small surface area and low removal efficiency, it falls short of activated carbon. By connecting β-CD and aromatic groups, they created the P-CDP (β-CD-containing polymer) molecule, which has a large surface area and porous properties, and can effectively remove organic micropollutants even in flow-through reactors too. The polymer can be regenerated several times without losing its effectiveness, and its effectiveness is many times that of activated carbon, it effectively removed many organic micropollutants (pesticides, drug residues, bisphenol) in ambient concentrations. The use of cyclodextran is not yet widespread, but it is showing promise in the removal of organic micropollutants.

5.4.2. Biological Removal Processes

During biological wastewater treatment, biodegradation is the dominant organic micropollutant removal method. Biodegradation of micropollutants can take place by two main mechanisms, namely metabolism and cometabolism. In wastewater treatment systems, most organic micropollutants do not enter the anabolic or catabolic pathway of microbes, but the microbes build their cells by using the growth substrate found in the environment, and by the way, they enzymatically transform the micropollutant into a molecule that another member of the microbial consortium is already able to metabolize and to be used as a growth substrate (cometabolism). The removal of organic micropollutants by biodegradation in wastewater treatment plants showed a positive correlation with high ammonium oxidation activity, presumably due to the broad metabolic spectrum of nitrifying bacteria.

As mentioned, the reduction of the real organic matter content takes place in the second step. For this, biological cleaning units are generally used, in which the biota (bacteria and protozoa) use the pollutants as a substrate during their metabolism. Secondary sewage treatment plants can be fixed-bed or suspended systems.

- The essence of the fixed-bed or fixed-film treatment methods is that the biological cleaning takes place in the biofilm formed on the substrate. The carriers can be inert (stone rubble, gravel, sand, polyurethane foam) or materials with ion exchange capacity (e.g. zeolites, activated carbon). In the case of the latter, in addition to biodegradation, pollutants are also filtered out through sorption processes.

- Although fixed-bed reactors are capable of greater efficiency, activated sludge systems, which require less space and can be operated more economically, are more widespread as the second stage of biological wastewater treatment. In these, the microorganisms are mixed with the wastewater, and the primary scene of biodegradation is the flakes formed by bioflocculation. With the activated sludge method, a reduction of approximately 90% of organic matter can be achieved, which manifests itself as a proportional increase in biomass.

5.4.3. Chemical Removal Processes

During the most typical wastewater treatment processes, organic substances and pathogens may remain in the treated wastewater, for which oxidizing agents are used to remove and disinfect the water. The most frequently used chemicals and oxidation methods are chlorination, ozonization, hydrogen peroxide and chlorine dioxide. Modern oxidation processes (Advanced Oxidation Processes - AOPs) remove toxic organic pollutants more efficiently than traditional disinfectants, but they are not equally effective for all micropollutants. AOPs typically use strong oxidizing agents alone or in various combinations, such as hydrogen peroxide ($H2O2$), ozone ($O3$), catalyst (iron ion, electrodes, metal oxides), radiation (UV, sunlight, ultrasound). These processes are used both before and after biological treatment depending on the type of pollutants to be removed. In the first step of AOP processes, reactive oxygen species, usually hydroxyl radicals (OH·), are formed. These strong oxidizing agents react with hard-to-degrade organic pollutants dissolved in water and can result in their oxidation and relatively rapid degradation. O3 is able to chemically degrade pollutants either directly or indirectly by generating the OH· radical. A disadvantage of the procedures may be that during the chemical transformation, the molecule is not broken down, but turns into a more toxic transformation product (Knisz et al 2020).

6. Biological parameters

6.1. Coliform, Escherichia coli, Enterococcus, Colony count 22°C

Faecal indicator bacteria like total coliforms, faecal coliforms (thermotolerant coliforms), E.coli and intestinal enterococci (faecal streptococci) are excreted by humans and warm blooded animals, pass sewage treatment plants to a great amount and survive for a certain time in the aquatic environment E. coli and faecal coliforms are the best indicators for the assessment of recent faecal pollution, mainly caused by raw and treated sewage and diffuse impacts e. g. from farm land and pasture. E. coli and faecal coliforms indicate also the potential presence of pathogenic bacteria, viruses and parasites. (Kavka & Poetsch 2002). The concentrations of heterotrophic bacteria (heterotrophic plate count 22°C, colony count 22°C) correspond commonly with contamination by organic matter (Kohl 1975).

The occurrence of coliform bacteria in otherwise high-quality drinking water has been the nemesis of the water industry. The occurrence of these indicator organisms in the absence of contamination leads to false alarms regarding microbiological water quality. These false alarms tax the ability of water utilities to respond to the problem, try the resources of regulatory agencies, and undermine the confidence of water consumers. Even more serious, growth of coliform bacteria in potable water supplies may mask the presence of indicator organisms resulting from a true breakdown of treatment barriers. (Le Chevallier et al. 1990).

Among the pathogens disseminated in water sources, enteric pathogens are the ones most frequently encountered. As a consequence, sources of fecal pollution in waters devoted to human activity must be strictly controlled. Entero-pathogens, such as Escherischia coli O157:H7, are generally present at very low concentrations in environmental waters within a diversified microflora.

Most coliforms are present in large numbers among the intestinal flora of humans and other warm-blooded animals and are thus found in fecal wastes. As a consequence, coliforms, detected in higher concentrations than pathogenic bacteria, are used as an index of the potential presence of entero-pathogens in water environments. The use of the coliform group, and more specifically E. coli, as an indicator of microbiological water quality dates from their first isolation from feces at the end of the 19th century. Coliforms are also routinely found in diversified natural environments, as some of them are of telluric origin, but drinking water is not a natural environment for them. The use of the coliform group as an indicator of fecal contamination is subject to strict governmental regulations. E. coli is the most common coliform

among the intestinal flora of warm-blooded animals and its presence might be principally associated with fecal contamination. No E. coli are therefore allowed in drinking water (Annie Rompré et al. 2002).

Enterococci may be considered an obligatory part of the intestinal cavity of humans and animals. Therefore, these bacteria have been useful as indicators of poor hygiene in water and in foods. However, the use of enterococci as 'hygienic indicators' requires better knowledge of their microbial ecology. For example, E. faecium is widely distributed in the intestines of humans and other animals, whereas E. faecalis is more generally associated with humans. However, both species are widely distributed in the environment and they are also associated with plants. In vegetable foods, interpretation of enterococcal findings is difficult because many strains remain undefined and because species of plant-associated enterococci, such as E. mundtii or E. casseliflavus may occur together with enterococci of faecal origin, such as E. faecalis or E. faecium. With this wide distribution it is not surprising that enterococci occur in different foods, especially those of animal origin.

The value of most Enterococcus spp. as indicators of faecal contamination of foods is also limited by their ability to survive in adverse environmental conditions such as extreme pH, temperatures and salinity. This means that these bacteria could withstand normal conditions of food production. Therefore, although enterococci remain good indicators of faecal pollution in drinking water and some dairy products, such as yoghurt, butter and milk powder, they can be considered as faecal indicator organisms in other foods only in a broad sense because the occurrence and significance of their presence may vary according to the species, the habitat, and the technology of food production. (Giraffa et al. 1999).

The rationale for routine microbiological monitoring usually includes the tests of colony counts at 20–22°C and 37°C. Large numbers of micro-organisms occur naturally in both ground and surface waters, many of which are associated with soil and vegetation and can survive for long periods in the environment. Counts of such organisms, grown as colonies on or in nutrient agar, provide a useful means of assessing the general bacterial content of a water. The colony count, or plate count, following incubation at 20–22°C gives an indication of the diversity of bacteria present at normal environmental temperatures. Although the result does not have any direct health significance, it provides a useful means of assessing the efficacy of the various water treatment processes in terms of overall bacterial removal. It also gives an indication of the general microbiological state of a given distribution system. (Ratnayaka et al. 2009).

Different strains of bacteria are normally present in natural waters. The bacterial strains tested in this project are found in significant quantities in samples taken after wastewater treatment plants. Higher levels were observed in some cases after discharge into the Mura River, but without significant changes in its quality. The coliform bacteria group is an indicator of faecal contamination. Bacteria counts were extremely high at two influent points. The prevalence of E. coli and Enterococcus bacteria showed the same trends as the coliform group.
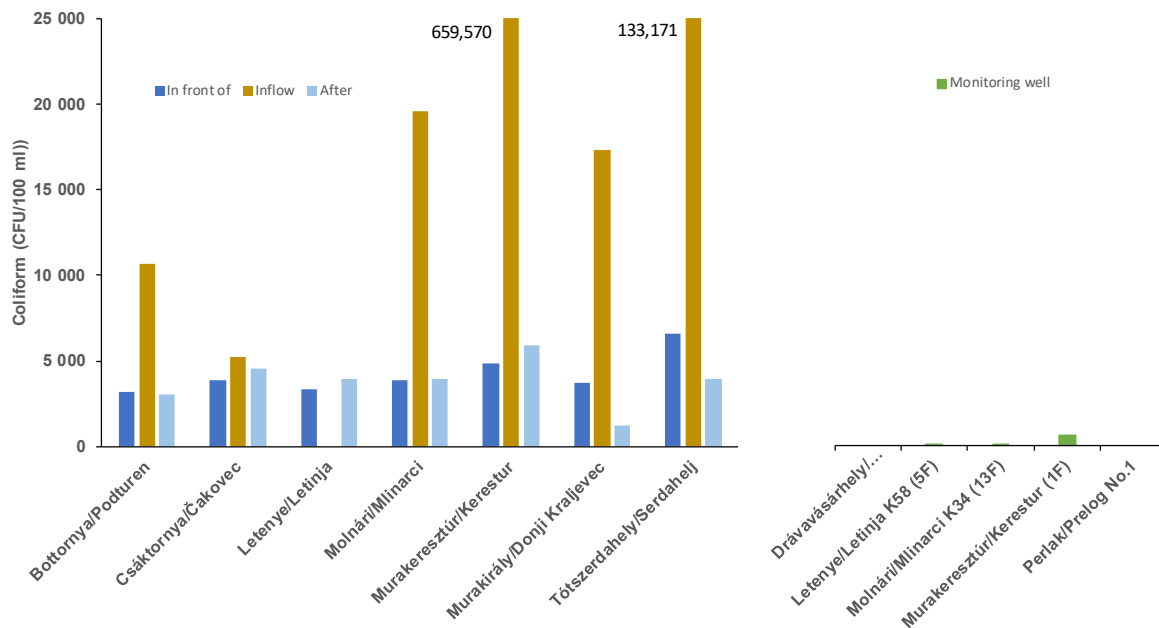
The change of Coliform bacteria during the investigated period
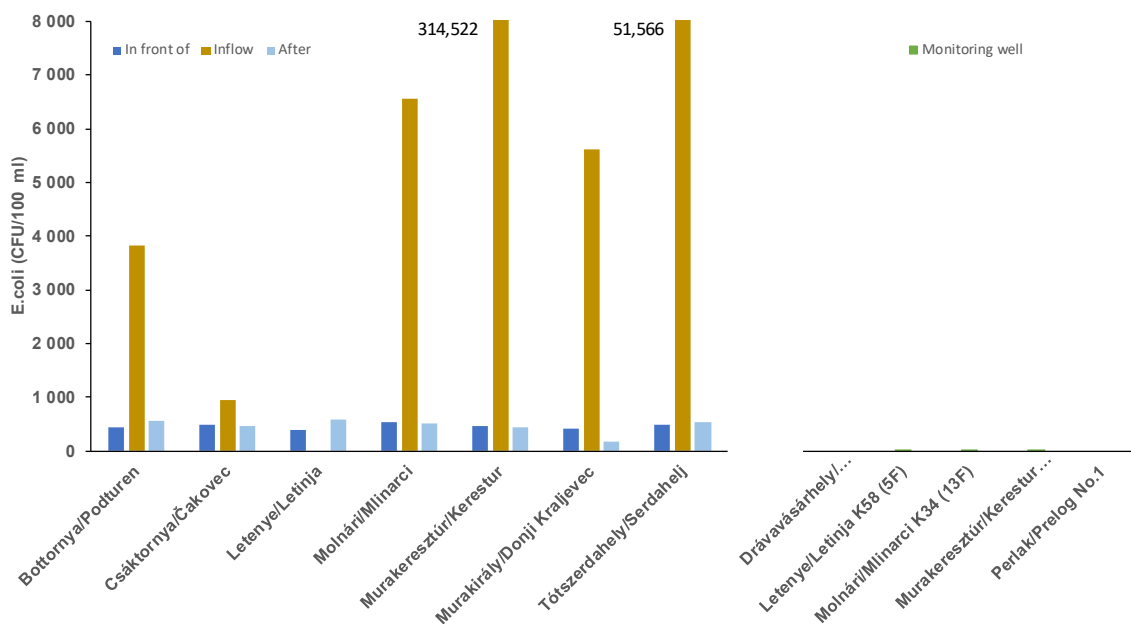
The change of E. coli bacteria during the investigated period
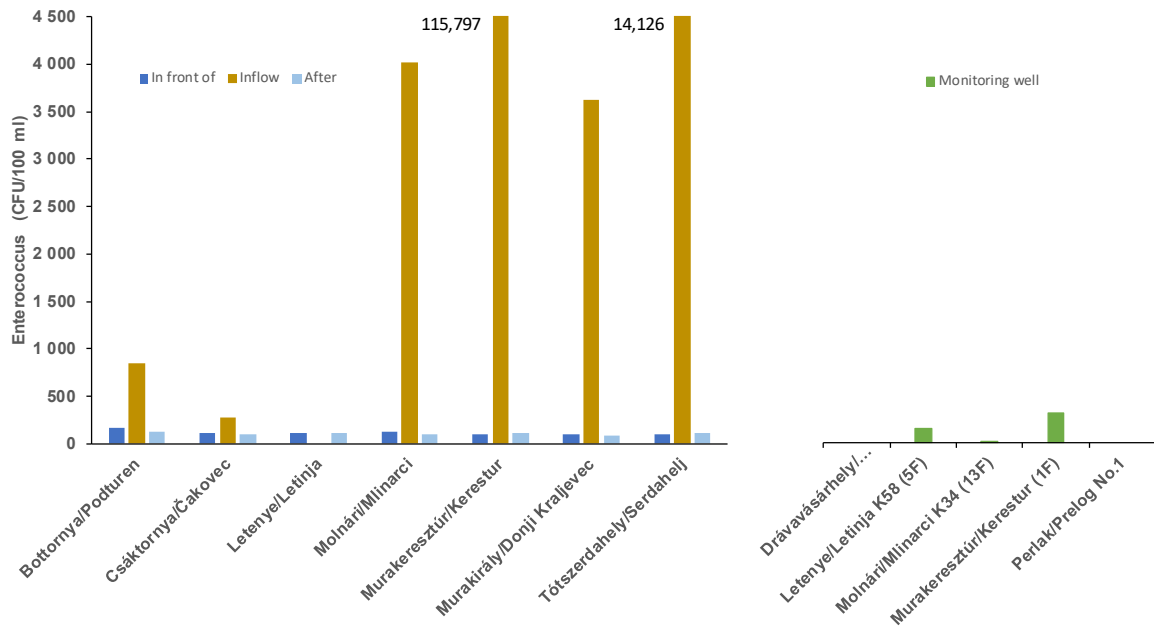
The change of Enterococcus bacteria during the investigated period
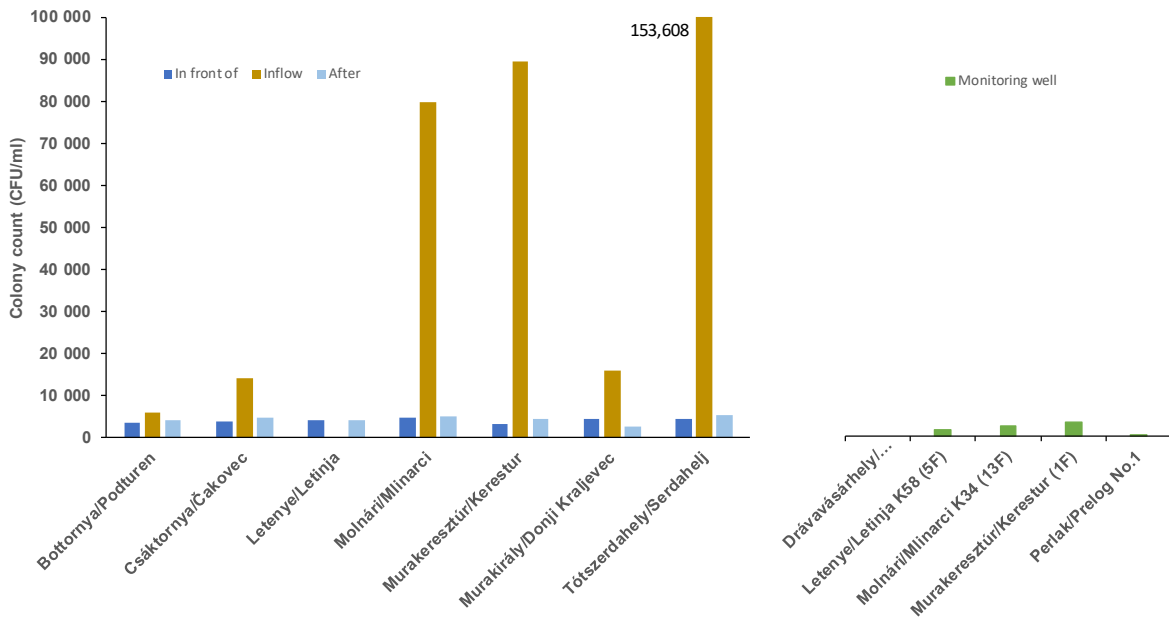
The change of colony counts of bacteria at 22°C during the investigated period

6.2. Disinfection methods

One of the most important parts of drinking water treatment is disinfection, which aims to reduce the number of micro-organisms below the specified level.

The demand on disinfection methods:

- small quantities, high efficiency in the removal of micro-organisms,
- have a long-lasting effect (until the water reaches the consumer's tap),
- preferably avoid the formation of by-products that would affect the water quality in an unpleasant way,
- do not react chemically with any substance other than micro-organisms.

6.2.1. Chlorine

In Hungary, the most commonly used disinfectant in drinking water treatment is chlorine, which is used in the following forms:

- chlorine gas (Cl_2),
- chlorinated water,
- hypo (NaOCl solution),
- chlorine lime.

Chlorine gas added to water reacts with the water in the following equilibrium reaction forming hypochlorous acid and hydrochloric acid:

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^-$$

The resulting hypochlorous acid dissociates as a function of pH:

$$HOCl \leftrightarrow H^+ + OCl^-$$
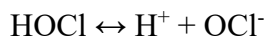
Chlorine in water is therefore not only soluble, but also hydrolyses and dissociates depending on the pH. In the reaction equations, Cl_2 is the gaseous chlorine, HOCl is hypochlorous acid, OCl^- is hypochlorite. The relative amounts of these three bactericidal oxidants depend on the pH of the solution (Öllős, 1987).

If the pH increases, and the concentration of H^+ ions decreases, the system tends to produce more hydrogen ions, so the process is shifted towards dissociation (more and more hypochlorous acid molecules are converted into hypochlorite ions). Undissociated hypochlorous acid has a stronger effect on microorganisms, so it is in our interest to use lower pH values for disinfection. The pH reduction is limited by the fact that the risk of corrosion increases at pH values below 7, which is why water with a pH below 7 should not be fed into the network. The pH range to be used for chlorine disinfection is therefore between 7 and 7.5.

Above pH 7,5, hypochlorite ions are formed in significant quantities, thus reducing the effectiveness of disinfection.
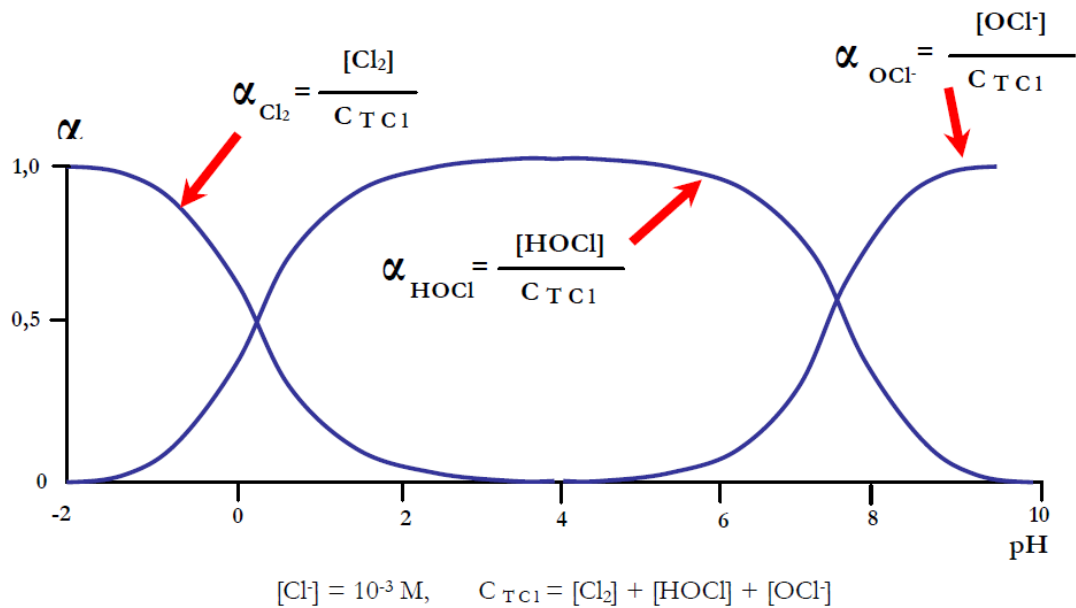
Balance of chlorine, hypochlorous acid and hypochlorite ions as a function of pH (Source: Öllős, 1987)

Hypochlorous acid oxidizes some of the oxidizable substances in water. For example, iron (II) compounds are oxidised accordingly, so the addition of chlorine gas facilitates the iron removal process.

Chlorine also reacts with the ammonium ion in water according to the following equation:

$NH_4^+ + HOCl \leftrightarrow NH_2Cl + H_2O + H^+$
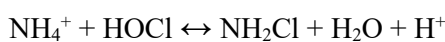
The resulting monochloroamine (NH_2Cl) has a very weak disinfectant effect.

If hypochlorous acid is in excess, it also reacts with the previously formed monochloroamine to form dichloroamine ($NHCl_2$), which is converted to trichloroamine (NCl_3) if there is a further excess of hypochlorous acid.

$NH_2–Cl + HOCl \leftrightarrow NHCl_2 + H_2O$

$NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O$
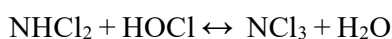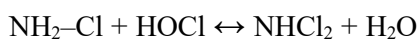
Therefore, in the presence of ammonium ion, a significantly higher amount of chlorine (hypochlorous acid) must be added to the system.
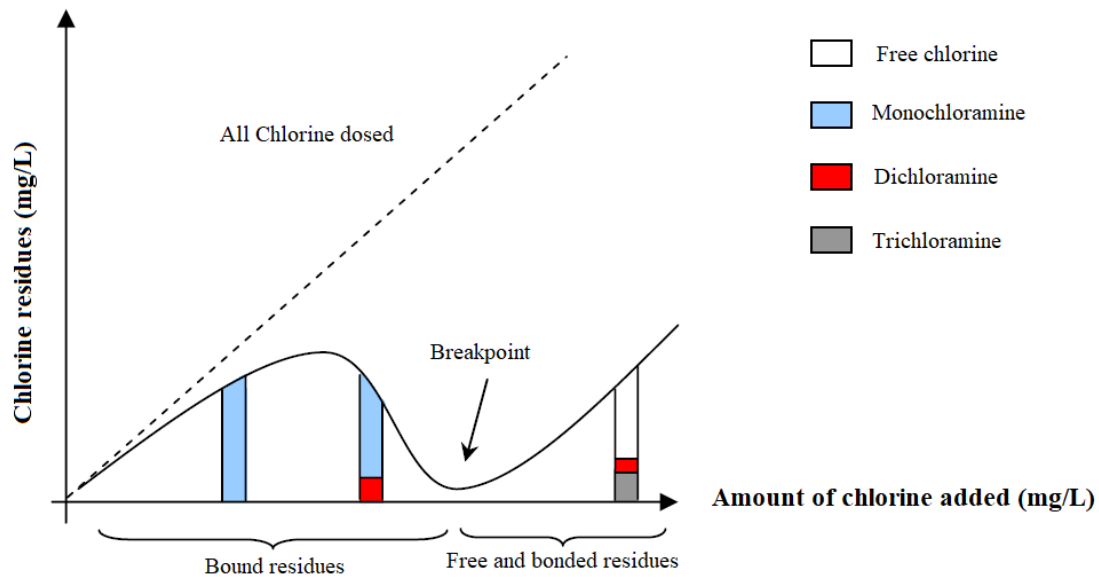
Breakpoint chlorination curve (curve expressing the reaction between chlorine and ammonium present in water)(Source: Öllős, 1987)

Chlorine can react with organic pollutants released into surface or subsurface water bodies as a result of human activity, as well as with some groups of naturally occurring organic substances, to form THM (trihalomethane) compounds that can cause cancer.

The formation of THM compounds is particularly likely in waters containing naturally occurring humic, fulvic and lignin substances in concentrations of a few mg/l.

Chlorine added to water for disinfection purposes also reacts with other organic substances, such as phenols and phenol derivatives released in industrial wastewater, to form chlorophenols, which can cause an unpleasant odour at concentrations of a few ug/l.

Chlorine as a disinfectant should be used with great care. The quality of the water to be disinfected has a major influence on the risk factor for chlorine use. In the case of waters containing relatively high levels of ammonium ions or organic matter, in particular, great caution should be exercised with regard to the conditions under which disinfection takes place.

6.2.2. Ozone

Ozone is an extremely strong oxidising agent, and even low concentrations are dangerous to living organisms, including higher organisms such as humans. Its disinfectant properties date back to 1886. Since then, researchers have studied the potential applications of ozone, but the use of cheap and effective chlorine has overshadowed the use of ozone and prevented its widespread dissemination (Langlais et al, 1991).

Initially, ozone was mainly used for disinfection purposes, but it was soon recognised that, as well as inactivating microorganisms, it also significantly improved the taste and smell of water. Ozone was also observed to have a positive effect on coagulation-flocculation processes, and was also found to be very effective in oxidising certain micropollutants.

It is produced from oxygen in air or from oxygen gas using high-voltage electrical discharges:

$3O_2 + E \leftrightarrow 2O_3$
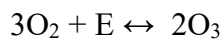
The extremely strong oxidising effect of ozone is due to the release of nascent oxygen.

$O_3 \leftrightarrow O_2 + ,O'$
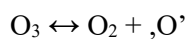
If this nascent oxygen cannot find a substance to oxidise, it is immediately converted by another nascent oxygen into a diatomic oxygen molecule with a relatively weak oxidising effect.

$,O' + ,O' \leftrightarrow O_2$
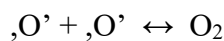
These reactions are the reason why ozone (once it is added to water) cannot exert its strong oxidising properties for a long time.

The disinfectant effect of ozone depends on the current pH of the water. At pH values higher than 8.0, very reactive hydroxyl and organic radicals can form in the water in the presence of ozone and organic substances. These highly reactive hydroxyl and organic radicals catalyse the decomposition of ozone and the oxidation of organic substances, reproducing themselves. In a slightly acidic environment, ozone oxidises relatively slowly but selectively. Oxidation in mildly acidic conditions is more favourable for the destruction of microorganisms.

However, in the pH range most commonly used for water treatment ($7.0 \leq pH \leq 8.0$), spontaneous ozone decomposition and non-selective oxidation of organic matter are dominant. This is the reason why ozone alone cannot be used as a disinfectant.

After leaving the water treatment plant, the treated water is discharged into the network, where it takes several hours to reach the consumer's tap. However, as ozone oxidises non-selectively, it is degraded within 1-1.5 hours after ozonation and its presence in the water is undetectable.

However, in the absence of a disinfectant, micro-organisms can proliferate in the network, causing secondary contamination.

In the first phase of ozonation, ozone does not react with micro-organisms but with other compounds in water, including organic matter. Ozone can break down high molecular weight organic substances and convert them into smaller compounds. These smaller organic compounds are now readily available to microorganisms, which can then proliferate in the water distribution network. This property, combined with the instability of ozone, may make it unsuitable for use in certain cases. As ozone readily transforms or reacts with compounds in water, effective residual ozone concentrations in the water distribution system cannot be maintained. In addition, if the organic matter content of water is high, high concentrations of organic matter (BDOC, AOC) available to microorganisms are formed as a result of ozonation (Albidress et al, 1995).

Since the application of secondary disinfectants after ozone application is also necessary, knowledge of the reactions between the secondary disinfectant and the by-products of ozonation, the resulting compounds and the public health effects of these compounds is also necessary. A possible solution is to use ozone as the primary disinfectant and then to add chlorine to the water distribution network to prevent deterioration of water quality.

Regarding disinfection by-products, the issue of bromate formation as a result of ozonation has been particularly prominent in recent years. Bromate is a carcinogen that can be formed from bromide ions as a result of ozonation and its formation is influenced by a number of water quality parameters. Therefore, in plants where bromide is present in the raw water and ozone oxidation is applied, it is of utmost importance to test the bromate content of the treated water.

6.2.3. Chloramine

Although chloramine is less effective than the previously mentioned disinfectants in killing both bacteria and viruses, it is very effective in keeping micro-organisms at a specific, low level. It is able to retain its disinfectant effect for a long time. It does not react with organic substances or ammonium ions. Accordingly, it retains its limited disinfecting capacity for a long time and does not produce substances harmful to health.

The disadvantage of monochloramine is that it adds a slight, but unpleasant odour to water. This is the reason why its use in combination with ozone, has not been widespread. However, there are waterworks that use ozone for the main disinfection process and monochloramine

produced on site for the post-disinfection process. Chloramine is produced by the reaction of ammonium sulphate and sodium chloride.

6.2.4. UV (ultraviolet) radiation

In a certain wavelength range, ultraviolet radiation has a strong disinfecting effect. This type of disinfection is not chemical, but physical, and deactivates the

microorganisms. The UV light is absorbed by the DNA of the cells, which modifies the bonds between certain base pairs in the DNA. The most significant aspect of disinfection is the dimerisation of thymine nucleotides as the thymine dimers formed prevent the DNA strand from being read, thus halting DNA replication and cell division.

The effectiveness of disinfection does not depend on the pH of the water being treated. Disinfection by UV radiation does not produce harmful by-products and the effectiveness of the treatment is not affected by the presence of ammonium or other ions.
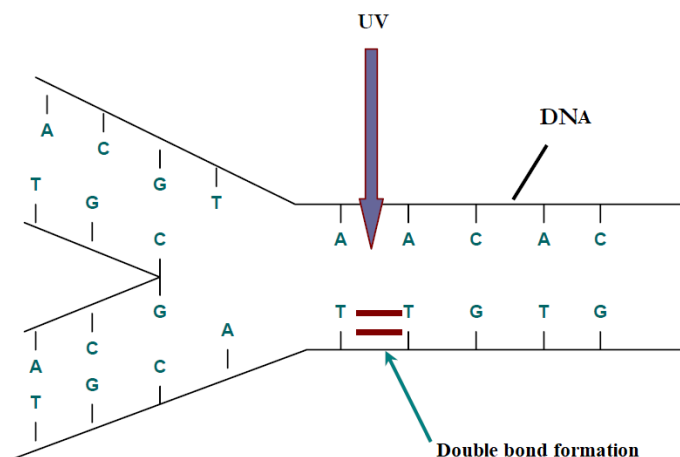
The mechanism of disinfection by UV radiation (Source: Öllős, 1987)

But ultraviolet radiation can only have the desired disinfecting effect in a few centimetres of water. The disinfecting effect of radiation can only be exerted for the duration of the radiation, it cannot prevent the growth of micro-organisms in the water network. Therefore, as with ozone and chloramine, it can only be used as a disinfectant in combination with other substances in the mains drinking water supply.

6.2.5. Membrane technologies

By applying high pressure to a membrane with the right pore size (nanometre scale), small molecules from solutions can be squeezed through the membrane, while large molecules remain in their original position. In essence, molecular separation is achieved by this process.

Given that the size of the microorganisms is significantly larger than the size of the molecules of the solutes, membrane technologies, in addition to molecular separation, also keep the microorganisms in their original location, they do not pass through the membrane with the purified water. Thus, reverse osmosis (or nanofiltration) has an essentially disinfectant effect. Unlike chemical processes, disinfection is not chemical but physical.

7. Conservation status of bird protection areas

The increasing trend of urbanization has resulted in considerable loss of biodiversity (Melliger et al. 2018), including birds (Aronson et al., 2014), leading to either local extinctions (Slabbekoorn, 2013) or various species adapting towards their altered habitats (Møller et al. 2012). Being highly visible and active, birds are considered as excellent indicators of environmental changes (Savard et al., 2000) and a robust assessment of mere presence/ absence information pertaining to a species or groups of species can be extremely meaningful.

There are so many animals in the world in need of protection. How do we decide which have the most critical need? Currently, the best way is to review an animal's conservation status. What is conservation status, you ask? Conservation Status is a hierarchical ranking, based on the severity of risk to a species' population (https://www.reclaimedearthwildlife.com/post/what-is-conservation-status-and-why-does-it-matter). The EU Habitats Directive (https://ec.europa.eu/environment/nature/legislation/habitatsdirective/index_en.htm) protects European animal and plant species, which are endangered, vulnerable, rare and endemic. The Directive also protects several natural and semi-natural habitat types. EU Member States report on the conservation status and trends in species and habitats within each biogeographical and marine region every six years. Additionally, such reporting collects comprehensive data on pressures and threats, conservation measures and the role of Natura 2000 sites. This information is then used to assess the implementation of the Directive and the progress in implementing the EU Biodiversity Strategy.

In term of birds, the migratory period is the most varied in autumn and spring, when *Ardea cinerea* and *Ardea alba* flocks congregate at the backwaters and they may overwinter in mild winters. On the open water *Anas crecca* and *Bucephala clangula* can be seen in winter. *Pandion haliaetus* is a frequent visitor to fishing lakes and mining lakes in April and September, in addition *Haliaeetus albicilla* is visible all year and also nests along Mura River. Backwaters provide a great nesting ground for *Tachybaptus ruficollis* and *Gallinula chloropus*, while *Charadrius dubius* feels best on plant-free gravel reefs (Bódis et al., 2008). The banks in the area provide excellent habitat for nesting *Merops apiaster*, *Alcedo atthis* and *Riparia riparia*. Of these species, *Alcedo atthis* can also be found in winter, sitting on branches, hunting for small fish.

Haliaeetus albicilla (source: https://www.europamadarai.hu/reti-sas/)

Alcedo atthis (source: https://ebird.org/species/blekin1?siteLanguage=cs)

Some of the components measured at the sites do not pose a short-term threat to wildlife, but the accumulation in fish and aquatic insects is the most alarming at high concentrations. Migratory and resident birds may also be affected by contaminants taken in from feeding, but chicks are more likely to be at risk.

The amount of heavy metals ingested during growth can cause changes in the morphology of the birds, resulting in the raising of less viable adults. High copper intake, for example, has a negative effect on kidney development but a positive effect on claw development (Albayrak et al., 2021). These changes may vary between species and even between genders, depending on the component that is more concentrated and available in the area.

Among adults, smaller species are more exposed to the risk of certain elements due to their higher metabolic rate than larger species. Studies have shown that ingested pollutants can be higher than by liquid intakes, and therefore predators are more vulnerable to these elements (Liu et al., 2015).

So ingested heavy metals are the most serious threat due to accumulation in aquatic organisms. However, the accumulated components in fish pose a low threat to the birds that consume them, such as Ardea cinerea. Birds that feed on sediment, however, are at greater risk from the heavy metals that are easily sedimented (Akila et al., 2022). However, none of the components measured in water during this project approached the levels measured in the above-mentioned studies.

The reproduction of our migratory and resident birds is influenced more by the accessibility than the quality of food, which can be aquatic organisms or sources of insects and other plants living on the gravel banks. In addition to food, the amount of potential nesting areas also has a major impact on the life of birds. However, these factors are most influenced by human construction/destruction (e.g. fishing, tourism, environmental changes) and action plans are being developed to address these problems, involving several countries.

8. Acknowledgement

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