



BLURRED TIRE TRACKS

QUANTITATIVE DATA ON MICROPARTICLES FROM TIRE WEAR ON ROAD SURFACE WASHING INTO SURFACE WATER

Balázs Gyula Urbán, Csaba Máté Kassai, Nándor Mészáros
BMSZC Petrik Lajos Vocational High School

Referring to the sources of primary and secondary micro-plastics in the surface waters of the mainland previous research data shows that a significant proportion, at least 20% of the particles come from tire wear.

The development of micro-plastics sampling equipment, the laboratory processing of samples (e.g. separation of granules from other components), the elaboration of the most appropriate methods for the quantitative and qualitative determination of granules raises many scientific questions. At present, protocols covering all aspects of the process have not yet developed.

Our work on micro-rubber particles was done with a triple goal. After the detailed elaboration of our methodology, our observations were applied on a specific sample area, and finally, we also examined the possibility of elimination by applying test filters.

The sampling of sediment washed away from road surface was carried out by sediment trap, while in the case of streaming water we worked with methods published by WESSLING Hungary Kft. which means that a large number of pumps and filter lines suitable for on-site water rotation were used. Parallel to field studies, we tested the effectiveness of filtration and separation under laboratory conditions, as well as the distribution of different fractions.

We chose our sampling area by the transparency of drainage from road surfaces, the easy accessibility of sampling points, the ability to break down the entire surface to sub-areas and the proximity of living surface watercourses. Based on these considerations, we chose the overpass at Pomázi Street and its immediate surroundings in Óbuda, where the highway stretches over the Aranyhegyi stream as it is on its way to the Danube. Here, rainwater collected from road surfaces feeds directly to the stream at several points. Samples were taken from the runoff waters, stream and channel sediments from selected sub-areas based on traffic characteristics such as traffic counting and driving dynamics data.

As a third direction, we dealt with the removal of the microbeads from the rainwater. With the permission of Bárczy Kft., we tested the filters developed by them in laboratory and field conditions. These filters are lined with oil-selective materials that are essentially water-permeable, so their use is not subject to a license.

We expect that our research experiences and measurement data will open up new, diverse research directions. So, later on, we would investigate the path of microspheres of other compositions, supported by instrumental analytics.



Keywords: *tire wear particles, Bárczy-filters, Aranyhegyi-patak, sampling of sediment*

INTRODUCTION

Among the sources of primary and secondary microplastics, the literature reports significant proportion of at least 20% of the the total amount of particles are derived from tire wear [1]. However the importance of the amount of rubber particles produced on the road surface and the precentage of those transported from the road and sedimented in rivers, streams and run offs which ultimately feed into larger water systems (larger rivers, lakes and possibly seas or oceans) is estimated rather than specific [2;3].

This is mainly due to the need for improvement in the sampling solutions for microplastics and rubber particles in particular and the need to improve laboratory processing of samples. Among other things, providing the correct amount of samples, seperating the particles from other ingredients/sediments then subsequently developing the most appropriate procedures for qualifing and quantifing the particles which raises many scientific questions. Currently, protocols covering all aspects of the process have yet to be developed.

In our longer-term project, we are trying to find answers to these questions. Our current work intends to be an introduction to this, in which we present our first measurement results in a selected sample area, along with sampling and laboratory methodological findings.

1.Site selection and characterization

Several aspects were taken into account when choosing the measurement site. The primary criterion was that rainwater should be drained from the road surfaces to live water. So we had to think of streams that crossed or parallel to streams or the Danube. It was just as important that the drainage system should be separate and transparent. In addition, it was important that the runoff sections be accessible to the water and transported sediment, that is, to be modeled.

As we want to show measurable differences in the volume of traffic and the dynamics of the traffic, this type of differentiation of the site was also important.

Based on these principles, our choice is the overpass of Pomázi Road and its immediate surroundings. Its located in Óbuda. The overpass and the surrounding roads as well as the drainage were constructed as part of the complete renovation of the Budapest-Esztergom railway line. It was handed over in spring 2016.

The entire structure of the bridge is 176 m long and crosses 9 pillars above the Aranyhegyi stream and the railway line. Traffic flows twice lane, as does the accompanying driving and detours. Traffic lights at each end of the bridge impede the smooth running of the bridge. Due to this latter situation, the tires may be more heavily loaded here.

The entire structure of the bridge is 176 meters long and rosses 9 pillars above the Aranyhegyi stream and the railway line. Traffic flows single lane in both directions as does the accompanying on slip roads and off slip. Traffic lights at either end of the bridge impede smooth operation of the bridge. Due to the latter situation the tires may be more heavily loaded here.

From the overpass pillar section, PVC (Ø160mm) fittings conduct rainwater down to the ground level trusses along the supports. Their run is free-end so sampling at these points is possible. From the sloping sections at the ends to the deep-level collectors running in the middle of the road, the water and sediment



of the sinks at the edges flow. By-pass catchment works similarly. After the mergers, the rainwater flows into the Aranyhegyi Stream at five locations without mixing with municipal sewage. An exception to this is the surface of the lead-in circular path, from where side drains lead to rainwater to the surrounding lower areas. The underground sewer system is accessible through the shafts in one or two places, so patterning is also possible here, beyond this we can only do this at the end of the pipe that runs through the slope of the stream ditch.

Based on these criteria, the chosen site proved to be appropriate for our research and sufficient in its dimensions.

2. MEASUREMENT AND SAMPLING METHODS

The improvement of sampling solutions for microplastics, such as rubber granules, the laboratory processing of samples, and the development of the most appropriate procedures for quantifying and qualifying granules all raise a number of scientific questions. Currently, protocol procedures covering all aspects of the process have not yet been developed. In our research, both new field observations and laboratory investigations of water and sediment samples required new observations. In the analyzes we also built on the methodology of traffic counting and the opportunities provided by GIS.

2.1 Field sampling

Solid particles, such as rubber particles, leached from road surfaces by rainwater can be sampled in two different matrices in two different media. On the one hand, from the flowing water and, on the other, from the sediment deposited at several points. In addition, significant differences in methodology may occur due to precipitation intensity. For example in the case of flood-like rainfall the sediment quantity in the water is almost odorless. The first results of domestic research on micro-plastics in surface waters were presented for the first time at a conference organized by WESSLING Hungary Kft in October 2018 [4]. We first heard about surface water body sampling developed by WESSLING Hungary Kft. We have also created a pump-filter system that can sample many m³ of water on site. With the exception that our filters operate with a filtration accuracy/efficiency of 150-90-50-20 micrometers. Some of our laboratory and stream water sample test measurements were made using these, and currently, in the absence of heavy rainfall, only measurable laboratory results can provide meaningful results.

Due to the extreme drought of early spring 2019, we were unable to sample rainwater. As a result, sediment samples washed away with minor rainfall were analyzed. Due to the small amount of rain, the ends of the tubes were sealed with a tipping system that prevents sediment outflow as opposed to small amounts of water. Accumulated sediment was almost completely recovered from most of the tube ends. In two cases, we could only partially sample the longer horizontal tube end.

As an additional sampling opportunity, we installed an oil-selective filter with the standard provided by Bárczy Kft. Installed devices will be periodically checked and analyzed for content.

Sediment sampling from the Aranyhegyi stream was performed with a telescopic dip. About half a kilogram of samples were obtained at each sampling site.

2.2 Laboratory tests

Due to the complexity of our work, we had to divide our tasks into three areas. We had to deal with the question of how efficiently we can separate the microparticles they pick from the types of filters we choose. In addition, the question was how to separate the elements of interest in the collected sediment samples. Finally, we had to find a solution on how to identify the detached micro rubber pieces.



2.2.1 Test measurement, system efficiency measurement

We have made our own filtering system based on our professional history. But since this was partly different from the previous modeling methods, we had to make sure its effectiveness. We did this with an artificial sample by gravimetric measurement. This sample was made of several car tires which were filed with a rasp. The grated sample was measured on an analytical balance. The initial weight of our sample was 1.0069 g, which is what we added into the filter system. During the measurement, the same filter series was used as in the field sampling (150-90-50-20 μm). The weighed rubber pieces were mixed into the buffer tank and pumped with continuous stirring and addition of water. During this time, 500 liters of water were circulated through the system.

After the filtration phase, the filter pads were cleaned using pipettes and brushes. The filtrate was pelleted in an Imhoff dish for 3 days. The floating and settling elements were then filtered off with filter paper. The samples were dewatered in an oven, keeping in mind the ideal standardized drying temperature (105 ° C). Thus, neither the paper nor the sample is damaged or has lost material.

Table 1: Results of the test measurement

	A	B	C
1	Fraction	weight (g)	
2	150 settling	0,909	
3	150 float	0,021	
4	90 settling	0,0348	
5	90 float	-	
6	50 settling	-	
7	50 float	-	
8	20 settling	-	
9	20 float	-	
10	All	0,9648	95,82%
11	Original	1,0069	100%

The samples were weighed individually on an analytical balance and the weights combined. We tabulated these and then calculated how much we could recover from our initial sample. The starting weight was 1.0069 g and the recovered weight was 0.9648 g. It follows that 95.82% of the rubber particles could be detected from the initial 100%. Based on these we can say that this measuring method is approximately 96% true, in that possible to detect the rubber particles in the crude samples with such accuracy and to recover them from the filter surfaces.

2.2.2 Preparation and separation of sediment samples

Our goal is to extract rubber pieces from sediment samples, which takes a lot of time and labor, and the process itself is based on a physical density difference that can be performed in a simple laboratory environment with certain materials or tools. The first step is to prepare the sediment samples taken from the target area. The next step, after drying at 105 ° C, is to determine the mass of the samples in grams using a flow balance. The sample thus obtained is placed in a large 1L beaker and topped with water so that the plant parts, as well as substances lighter than water, float to the surface.

To the remaining sediment samples is added 1 mol / dm³ of hydrochloric acid while stirring under a chemical booth to react with and eliminate most of the carbonate rocks (limestone, dolomite) contained therein. (this takes about an hour or two).

The resulting hydrochloric acid-treated sample was partitioned with a solution of Fe (III) chloride at a density of 1.3 g / cm³, resulting in a precipitation of rubber particles (with continuous agitation) and floating to the surface due to the density of the rubber. with a density of approximately 1.2 g / cm³.

The difference between the floated and sedimented materials is clearly visible and can be separated, thereby separating the upper and lower layers and filtering them with filter papers, just as in the case of floating parts. These floated portions are washed with filter paper, placed in an oven, and dried at an ideal temperature. In this case, this means 105 ° C for about half an hour, so that the filter paper does not burn and the rubber content of the sample is not damaged.

The working solution and hydrochloric acid will destroy the filter paper material. However it should be noted that the rubber pieces are not destroyed by the materials mentioned in the process. The tires were also tested with concentrated hydrochloric acid and ferric chloride solution for several days. After soaking for several days, the pieces were re-examined and showed no change in material or make up.

2.2.3 Microscopic examinations

After our samples were prepared live, which means that we reduced their organic content, removed the asphalt fragments from the heavier elements, and removed the carbonate particles with hydrochloric acid, the search for rubber particles began. Others did this with spectroscopy [4] in the search for microplastics, but we found a simpler but safe method for car rubber pieces. In the prepared samples, the rubber particles were searched by stereo microscope. In fact, during our examination of the sample, we noticed that the rubber particles could be detected from other particles by physical and morphological methods.

The physical characteristics of the car tire are quite unique. they are different from other substances found in nature. Such is the flexibility. First we always identify them morphologically, we can do this by analyzing the specimens, and then the elasticity comes. We can do this very easily with the help of a needle. When one tries to compare a piece of quartz or the exoskeleton of a beetle with the elasticity of



a rubber particle, one soon realizes that the difference between the two is unmistakable. Rubber is probably the most distinguishable one from other particles because of its elasticity. However, there are times when, even without them, we are almost certain that we have found rubber in our sample. For example, when we encounter a small cylindrical piece on a new car tire in the eyepiece of a microscope, or when we find a centimeter long, well-identifiable rubber piece in our sample. Of course, in such a case, the examination of elasticity should not fail.

No.1 Picture: A piece of tire tread

2.2.4. Analysis of zinc content by instrumental analytical method

Besides microscopic morphological examination of microbubble particles, we also tried to find another method for the identification of the rubber material. Because we haven't been able to identify organic ingredients yet, we've tried to detect some inorganic additives. During the vulcanization of the rubber material, relatively large amounts (1 to 2%) of zinc compounds [5] are used as catalysts. We were hoping to prove the rubber content of our granules with similar zinc content.

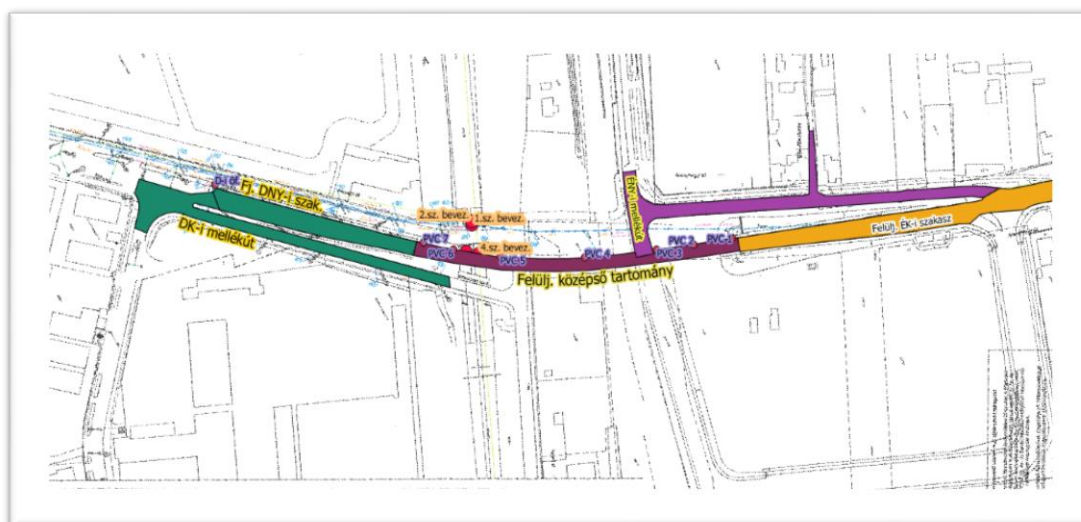
Our tests were carried out in the instrumental analytical laboratory of our high school. The morphologically selected particle assemblage (about 80 mg) was prepared by microwave assisted wet digestion (HNO_3 , H_2O_2) in a Teflon bomb. Full digestion of the sample was possible by double digestion. Atomic absorption analytical measurement was performed on a Shimadzu AA-7000 spectrophotometer.

The zinc content of our two samples was found to be between 0.05% and 0.065%, which is well below the literature data. During the digestion, the remaining carbon black content in the solution may have absorbed a significant amount of zinc on the surface of the granules, so this is probably the reason for the magnitude difference in the results. Further development of this method is contemplated, but other

instrumental analytical methods, such as thermogravimetry, may be used to determine the rubber material.

2.3 Geospatial analysis

The primary objective of our project is to provide quantitative data on rubber particles that are leached directly from the road surfaces, transported and settled. A significant factor in this is the size of each road surface. Various geospatial software programs help in the delimitation of subdivisions and the determination of dimensions. Of course, dimensional data is not geodetic accuracy, but it can be used to determine perfectly proportional values. In this work we used version 2.18 of the free and open source QGIS program. Terrain points were recorded with a Garmin e-trex 10 GPS receiver compatible with the above software and polar coordinate mapping using a LEICA Sprinter 50 digital leveler. The 1: 1000 scale basic map comes from the Metropolitan Sewerage Works repository. The Pomázi road overpass and the surface of the corresponding service roads were subdivided into subdivisions according to their role in the traffic and the sampling possibilities.



No. 1 Map: Units of the test area

The drainage relationships of the sinkholes and shafts in the south-eastern part of the area are completely clear from the basemap data, we have Df. at a point called a mine, the surface can be tested for water and sediment. In the north-east, the contact elements are not marked and will be determined later by a floating method in case of significant rainfall. However, it is already certain that from here the rainwater reaches the Aranyhegyi Stream through inlet pipes 1 and 2. At intake points 3 and 4, rainfall falling into the middle section of the overpass reaches the live water. With respect to the sub-surface area of nearly 7000 m², the average area of which is 1500 m², it should be noted that at least three mm precipitation/rainfall is required in a single occurrence to sample the rainwater flowing from them (1.5-2 m³ at times). The spatial data is numbered 2.

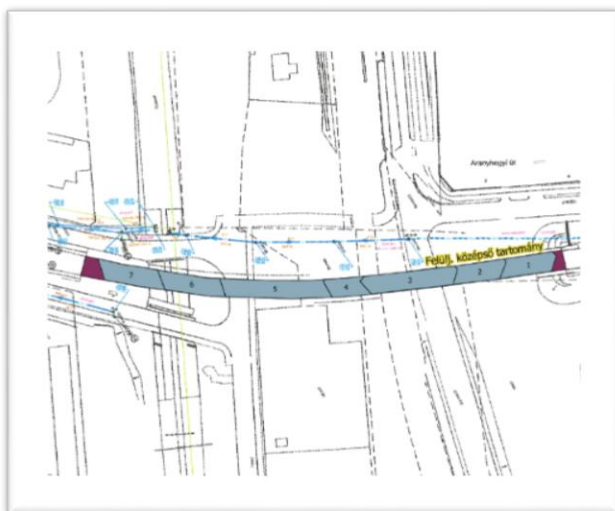
No. 2 Table 2: Size of road sections in m²

Names of road sections	The surface of road section (m ²)
Overpass Southwest Section	1025
Southeast side street	1348
Overpass middle range	1194

Overpass Northeast section	1739
Nortwest side street	1651
All test areas	6957

The middle section of the overpass can also be directly patterned using free-flush PVC duct elements along the bridge pillars. The smaller sub-areas belonging to each drain and their size are shown in map 2 and table 3.

No. 2 Map: Areas of drains



PVC drain pipe	subfield m ²
1	131
2	120
3	222
4	93
5	252
6	149
7	154

Table 3: Size of these areas in m²

3. EVALUATION OF RESULTS OF SEDIMENT SAMPLES

Our sediment samples were taken on the one hand from the drainage ends directly characteristic of the road surfaces and on the other hand from the section of the Aranyhegyi stream to the Danube.

3.1. The examination of sediment in drains

A total of 2 rows of samples could be taken from the drains. One on April 4, 2019 and the other on 3 days later on April 7, 2019. These were taken after both rains. There was rain 24 days before the first sampling, which would have washed the rubber pieces into the channels. The precipitation in this sample was 3 mm. For the second pattern, it only took 3 days for the rain to come, which brought 5 mm of water. These aspects will now be useful in the analysis because they are the basis for discovering the relationships in our measurement results. We took into account not only the weather factors but also the spatial distribution, slope and sewerage.

The results are summarized in the table below. The location, time, weather (precipitation) of the sample, and the results of laboratory measurements were also noted.

Table 4: Measurement results for sediment samples 1 and 2



A lefolyó sorszáma	A mintavétel időpontja	A mintázott hordalék tömege (g)	Bemosási esőmennyiség (mm)	Utolsó esős nap óta eltelt idő (NAP)	Gumiszemcsék száma
1	2019.04.06	70,00 (teljes minta)	3	24	N-2 K-0
2	2019.04.06	8,90 (teljes minta)	3	24	N-3 K-2
3	2019.04.06	1,22 (teljes minta)	0	24	N-0 K-0
4	2019.04.06	0 (teljes minta)	3	24	N-0 K-0
5	2019.04.06	12,50 (teljes minta)	3	24	N-1 K-0
6	2019.04.06	144,20 (teljes minta)	3	24	N-2 K-4
7	2019.04.06	57,50 (részleges minta)	3	24	N-0 K-0
Déli összefolyás	2019.04.06	42,40+44,5 (részleges minta)	3	24	N-1 K-0
1	2019.04.09	31,04g	5	3	0
2	2019.04.09	200,00g	5	3	15
3	2019.04.09	96,52g	5	3	16
4	2019.04.09	0,50g	5	3	0
5	2019.04.09	8,20g	5	3	8
6	2019.04.09	129,13g	5	3	12
7	2019.04.09	30,50g	5	3	7
Déli összefolyás	2019.04.09	100,00g	5	3	2

We then calculated the approximate number of rubber particles in each of the drains in 1000-1000 grams of sediment. There were quite surprising results, there was a drain that could hold 976 pieces up to 1000 grams. The results are shown in Table 5.

Table 5: Amount of rubber in 1000g of sediment

2019.04.06	alap	/db	1 kg	/ db
1	70,00	2	1000,00	29
2	8,90	5	1000,00	562
3	1,22	0	1000,00	0
4	0,00	0	1000,00	0
5	12,50	1	1000,00	80
6	144,20	6	1000,00	42
7	57,50	0	1000,00	0
8	86,45	1	1000,00	12
2019.04.09				
1	31,04	0	1000,00	0
2	200,00	15	1000,00	75
3	96,52	16	1000,00	166
4	0,50	0	1000,00	0
5	8,20	8	1000,00	976
6	129,13	12	1000,00	93
7	30,50	7	1000,00	230
8	100,00	2	1000,00	20

Knowing the values per unit, we could begin to deduct the conclusions. A drain that did not have a single piece of rubber in both samples, only one, drain 4. This point is in the middle of the bridge, with the smallest area from where it receives rain and descends in both directions. The smallest load on this section, or the rubber pieces that are deposited here, will be washed away down the drain. In a sample in which we found twice the significant amount of rubber, there were two. Based on the conclusion, they are likely to accumulate in drains 2 and 5 due to the flow of section 4. This is where the dirt and rubber pieces that accumulate there fall, so the proportion of rubber pieces in these samples is much higher. The drainage containing most of the particles was 5. It is one of the slopes of the bridge, which has a large rainfall flow and has the largest surface area of 252 m². Based on our measurements to date this is considered to be the part of the bridge with the heaviest accumulation of (tire) particles with 976 units

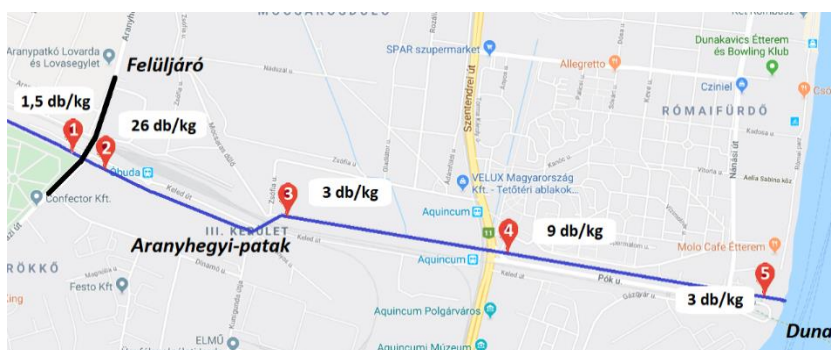
There is a large difference between the results of the two measurements which can be explained due to the weather. There was no rainfall for the 24 days prior to the first sampling meaning that a large amount of dirt accumulated, at the same time there was a relatively small amount of rainfall. This proved insufficient to completely leach the surface and wash the particles into the drainage system. Then for 3 days it rained more heavily which completed the leaching process and washed more particles into the drainage system giving a much higher sample yield to the second samples.

3.2. Examination of the sediment samples

From the overpass at Pomázi út, the run-off from the overpass flows into the built-up sewer system and from there to the Aranyhegyi stream. This is supported by our field observations and the channeling map provided by FCSM. In our study, sediment that was washed directly off the road surfaces contained rubber particles. We were right in assuming that rubber spheres would also enter the stream via spouts in the creek slope. With this study, we sought to determine the extent to which sedimentation of subsurface canalization works and the extent to which rubber debris is still present at certain points in the stream's approximately 2.5 km stretch to the Danube. A total of 5 sampling points were selected along the stream, averaging every 500 meters.

Our first sampling point is located in the stream upstream, about 10 meters from the influence points. The second is right after the overpass. In determining this, we considered it important not to take a sample directly below the lead-in point, as rubber particles settle more slowly in water that has increased and become turbulent. Finally, the sludge was sampled about 25 meters from the inlet pipe. The third sampling point was selected on the slower, calmer part of the stream. There is no replenishment here for car rubber particles to enter the stream water. The fourth sampling site was found just after Szentendrei út. According to the relevant FCSM map, rainwater flows from the main road into the main catchment below the stream bed, not directly into the stream. During our trekking, however, we found two rainwater drainpipes that carry water and sediment from the area around the train station into the stream. Our last sampling site was at the mouth of the creek, before any rubber replenishment was possible only at the crossing at the corner of Pók Street - Nánási Road.

No. 5 map: Sampling points of the Aranyhegyi stream



Sampling points of the Aranyhegyi stream. The samples were processed according to the methods discussed above, and the sediment rubber particle content was calculated per kilogram. At the first point before the influence, there is

an average of 1.5 car tires in 1 kg of sludge. On this basis, the stream is also polluted in the section in front of the overpass (eg at the so-called Üröm roundabout). At the second point, after the rainwater has been introduced, the sludge contains 26 particles per kilogram. This is our highest measured result. This is obviously a source of contamination, but the result is below the values at the end of the drain. Underground sedimentation basins thus partially fulfill their function.

At our third measuring point we found 3 pieces of rubber in 1 kg of mud. This reduced value indicates the possibility of rubber particles settling about 500 meters after the source of contamination. At our fourth sampling point, we found 9 particles per kilogram, an increase from the previous point. Since there is no supply from the surface of Szentendrei road, we can only blame the railway station for the slightly higher measured value. It is worth mentioning here that despite the many lanes of the Szentendrei road, despite the much higher traffic, the stream is not directly polluted, because from here the rain water is transported to the main catchment with the sediment it carries. At the last pre-Danube sampling point, 1 kg of mud contained 3 rubber particles. On this last few hundred meters there was another possibility of sedimentation. In summary, our results supported our assumptions:

- The car tire particles get into the Aranyhegyi stream from the overpass
- They are present in the sludge and settle continuously



- The 2.5 km stream cannot completely settle the rubber particles, so the Danube gets a microplate supply from here

SUMMARY

In our long-term project, we are now able to achieve significant results in the field of sediment leaching directly from road surfaces and in sample handling. We first use our skill in separating the types of material here by density and in identifying a few millimeters of rubber beads by examining changes in the amount of rubber fragments associated with weather, surface size, and drop.

By modeling the sediment of the about 2.5 km stretch of the Aranyhegyi stream up to the Danube, the rubber contamination of the live water from the overpass area and its transport to the Danube after settling became clear.

To confirm the material of the rubber particles separated from the sediment, we have begun an instrumental analytical study of zinc content, which requires further careful development.

REFERENCES

- [1] Hann, S.; Darrah, Ch.; Sherrington, Ch.; Blacklaws, K.; Horton, I.; A. Thompson Reducing Household Contributions to Marine Plastic Pollution, *Report for Friends of the Earth*, (2018)
- [2] K.M. Unice a,*, M.P. Weeber b, M.M. Abramson a, R.C.D. Reid a, J.A.G. van Gils b, A.A. Markus b, A.D. Vethaak b,c, J.M. Panko a Characterizing export of land-based microplastics to the estuary - Part II: Sensitivity analysis of an integrated geospatial microplastic transport modeling assessment of tire and road wear particles (2019)
- [3] K.M. Unice a,*, M.P. Weeber b, M.M. Abramson a, R.C.D. Reid a, J.A.G. van Gils b, A.A. Markus b, A.D. Vethaak b,c, J.M. Panko a: Characterizing export of land-based microplastics to the estuary - Part I: Application of integrated geospatial microplastic transport models to assess tire and road wear particles in the Seine watershed (2019)
- [4] WESSLING Hungary Kft <http://mikromuanyag.hu/> (2018)
- [5] E. P. Rhodes, Z. Ren, D. C. Mays: Zinc Leaching from Tire Crumb Rubber (2012)