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Measuring spatial and temporal variation of the chemical composition of suspended sediment of the river Rhine using a handheld XRF

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Abstract

The chemical variation of suspended sediment over space and time in rivers has rarely been studied. Moreover, measuring the chemical composition of suspended sediment in rivers usually requires the collection of large volumes of river water to obtain sufficient suspended sediment for analysis. In this thesis, the spatial and temporal chemical variation of suspended sediment in the Rhine River was studied using a handheld X-Ray Fluorescence scanner (XRF), since this device can measure element concentrations of suspended sediment extracted by filtering water samples. Because this approach is not widely used, the measured concentrations were verified with data obtained from the Dutch Ministry of Infrastructure and Water Management. The temporal and spatial variability in the Dutch part of the Rhine (Lobith – Oudendijk) was analysed by collecting synoptic and time-integrated suspended sediment samples. Moreover, fieldwork was carried out in the German Rhine (Basel – Rheinberg), to analyse the spatial variation of the chemical composition of suspended sediment and bed sediment. The concentrations measured from the water samples needed to be corrected, otherwise the concentrations between the differently obtained samples could not be compared. The temporal variability of the measured element concentrations provided a subdivision into three categories: (1) concentrations of Ca, Mn, and Zn declined with increasing water level and showed a negative relation with changing water height. The predominant process that explained this trend was dilution of point-sources from which these elements originated. (2) The concentration of Ti, Fe and Rb increased with increasing water height and showed a positive relation with changing water height. Remobilization of bed sediment into the stream due to erosion and reduced organic matter concentrations in the water were the main processes causing increased trace metal concentrations during high water events. (3) The concentrations of Cr, Cu, Sr and Pb in the suspended sediment showed no distinct reaction with respect to the increasing water level. The chemical composition throughout the Dutch Rhine showed little spatial variation. The concentrations measured in the suspended sediment in the German Rhine obtained by suspended sediment samples showed no major fluctuations and the concentration stayed relatively constant, whereas the bed sediment showed increasing concentrations in downstream direction. The measured concentrations in the bed sediment were substantially higher than the concentrations found in the suspended sediment at the same location. The main processes that caused the three major reactions in the chemical composition of suspended sediment in the Dutch part were dilution, remobilization and reduction of organic matter content.

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1 Introduction

The awareness of the environmental significance of the suspended sediment load transported through rivers and streams has been growing rapidly over the past few years (Walling, 2005). The main focus lies on the importance of the transport of nutrients and contaminants such as phosphorus, pesticides, heavy metals and pathogens with suspended sediment. Recognition of the wide-ranging environmental significance of fine sediment has generated a need for improved sampling and analysis methods in order to improve insight in variations of contaminant concentrations transported through rivers and streams. Trace metals are inorganic contaminants, found in very low concentrations (generally less than a few mg/kg) in the river system. The trace metals Silver (Ag), Titanium (Ti), Rubidium (Rb), Strontium (Sr), Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Iron (Fe), Manganese (Mn), Lead (Pb) and Zinc (Zn) are the most important contaminations. Some of these metals are essential for life of flora and fauna if they are taken up in low concentrations. Trace metals are toxic to humans if they are taken up in high concentrations (Miller & Miller, 2007). Trace metals tend to vary in terms of spatial and temporal distribution through the channel.

The Rhine catchment in particular is very suitable to investigate the variability of trace metal concentrations over space and time. The sediment flux in the catchment area of the Rhine is influenced by both natural processes (e.g. erosion and biochemical cycles) and human activities. The sediment flux and associated trace metal concentrations in the Rhine River increased due to anthropogenic landscape changes in the Rhine basin when the industry flourished. Until the early 1980s, industry was a major source of water pollution, until the ICPR created an action program to reduce the water pollution. The change of the sediment flux and corresponding changes in sediment concentrations of the river Rhine occurred at both the spatial and temporal scale and on different magnitudes (Stigliani et al., 1993). Alterations in the sediment composition are mainly the result of climate change, upstream land use change, environmental regulations and floodplain rehabilitation and therefore the concentration of trace metals are changing (Thonon, 2006). Another explanation of variable trace metal concentrations is the existence of sources and sinks along the river channel. Reintroduction of trace metals into the channel after sediment storage can occur on different timescales. During flood events the storage time of sediment sinks are relatively short, hours or days, until resuspension of sediment and thus trace metals occur. Without these flood events storage of trace metals in the bed sediment can last over a year (Owens et al., 1999). Many studies have shown that the sedimentation rates vary widely between floodplains (Lecce, 1997; Asselman & Middelkoop, 1998). These studies linked the variability of the sedimentation rate to upstream sediment delivery, suspended sediment concentrations, and the variability in flow characteristics within the floodplains. However, research concerning the variability of sediment composition in the river channel is hardly done.

Research on the spatial and temporal distribution and variation of the chemical composition of suspended sediment in river channels, including trace metal concentrations, is scarce. Furthermore, measuring the chemical composition of suspended sediment in rivers usually requires the collection of large volumes of river water to obtain sufficient suspended sediment for analysis. Alternatively, the separation of suspended sediments from the river water can be achieved using a continuous flow centrifuge in the field. A major disadvantage of centrifuging is that it does not recover the finest

sediment particles, which typically contain environmentally significant elements. Currently, a handheld X-Ray Fluorescence scanner (XRF) can be used to measure concentrations in obtained sediment, which is a relatively new and unknown measuring technique.

The objective of this research is to get a better understanding of the temporal and spatial variation of the chemical composition of suspended sediment that take place during transport in river channels. For this purpose, we tested the use of a handheld XRF, which requires a much smaller sample of suspended sediment (typically 5 – 50 mg) and, therefore, a much smaller volume of river water sample (< 2 litres). This was achieved by obtaining water samples and sediment samples for the Dutch and German part of the Rhine. The collected samples were scanned with the XRF and concentrations were analysed so that the following main question could be answered:

‘What is the spatial and temporal variation of the chemical composition of suspended sediment of the river Rhine?’

This main research question will be answered using the following sub-questions:

- Can the chemical composition of suspended sediment be determined from filtered manual water samples?
- If yes, is the chemical composition of the time-integrated suspended sediment samples (Phillips samples) comparable with the chemical composition of the suspended sediment extracted from the manual water samples?
- Is the chemical composition of the suspended sediment measured in the samples comparable with data measured by Rijkswaterstaat?
- What is the temporal and spatial variability of the chemical composition of suspended sediment in the Dutch part of the Rhine?
- What is the spatial distribution of the chemical composition of suspended sediment measured in the manual water samples and sediment obtained from the bed in the German part of the Rhine?

To answer the sub-questions and the main research question, field samples were collected from the river Rhine and its tributaries in the Netherlands and from the German reach of the Rhine from Basel to Lobith. The field samples were collected using three different techniques: the first technique involved a Phillips sampler that collects time integrated suspended sediment samples over a period of weeks. The second technique involved the collection of manual water samples which were filtered through a 0.45 µm membrane filter to extract the suspended sediment. Third, sediment from the bank of the river was taken in order to obtain the fine sediment by wet sieving the samples. The suspended sediment samples were analyzed for geochemical composition using a handheld XRF scanner. As XRF analysis of the sediment obtained with water samples is not a regular and established technique, this method requires testing and experimenting. The theory behind the handheld XRF scanner is presented in Appendix A. When this method was verified, the spatial and temporal variation of the chemical content of suspended sediment in both the German and Dutch part of the Rhine could be analyzed.

2 Site description

2.1 General

The river Rhine is one of the primary river systems of Europe with a total length of 1250 km and a drainage area of 185 260 km² which is distributed over nine countries. The countries that are situated in the Rhine catchment are Italy, Switzerland, Austria, Germany, Lichtenstein, France, Luxemburg, Belgium and the Netherlands. The Rhine provides several important services for the regions along the river and with an annual gross domestic product of approximately 1500 billion Euro, this area is one of the most important economical regions of Europe. Because of the economic prosperity in the region, approximately 60 million people live in the Rhine catchment of which many people live in large urban areas extending along the river between Basel and Rotterdam. Other important resources that the river provides are transportation, industrial production, power generation, agriculture, tourism, urban sanitation and drinking water for half of the inhabitants of the Rhine catchment. About 50% of the Rhine catchment is used for agricultural purposes, followed by forests (32%), urban areas (9%) and grassland (4%). In the Rhine Delta the primary land use type is agriculture with 60%, whereas in the Alpine Rhine and High Rhine this percentage is only 11% (Tockner et al., 2009).

The river catchment can be subdivided into six major river sections according to the classification of Tockner et al. (2009) and Disse & Engel (2001)(Figure 1). These river sections consist of (1) The Alpine

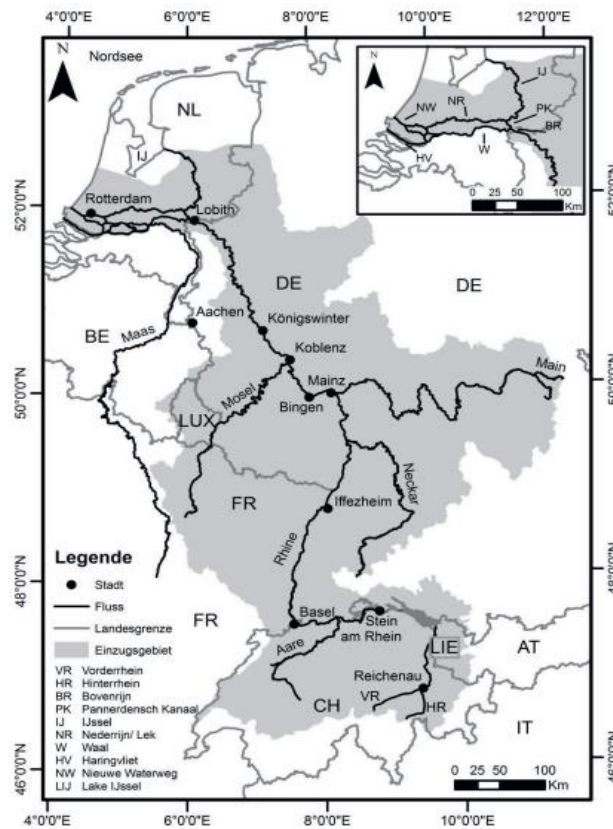


Figure 1: Catchment of the river Rhine and its main tributaries (Hillebrand & Frings, 2017).

Rhine and its tributaries which are located between the Lake Toma and Lake Constance, (2) The High Rhine that flows from Lake Constance to Basel where tributary the Aare flows into the Rhine, (3) the Upper Rhine where the Rhine flows through the Rhine Graben and the tributaries Neckar and Main confluences with the Rhine, (4) the Middle Rhine which breaks through the Rhenish Massif where the river has incised itself in the landscape creating a narrow valley and confluences with the Mosel river, (5) The Lower Rhine which meanders from Bonn to Lobith like a typical lowland with main tributaries Ruhr, Lippe and Emscher flowing into the Rhine and (6) the Rhine Delta where the river separates in the Nederrijn-Lek, IJssel and Waal distributaries.

2.2 Local geology

Rainwater contains very few dissolved ions. When precipitation reaches the surface and infiltrates, interaction with the soil and processes such as dissolution, sorption, plant uptake and concentration due to evaporation change the composition of the water. The main source of ions present in river water is the weathering and erosion of rocks and minerals. Therefore, the composition of elements in water reflects the geological setting in the drainage area (Van der Perk, 2006).

The most upstream part of the Rhine catchment, consisting of the Alpine Rhine and High Rhine, is predominantly composed of Mesozoic sedimentary rocks. The medium-scale rivers, Hinterrhein and Vorderrhein, drain the headwaters in the Central Swiss Alps. The source of the Hinterrhein lies in a crystalline nappe (i.e. a sheet of rock that moved sideways over neighboring strata as a result of folding) and with a basement consisting mainly of schists. The Vorderrhein flows through a valley with a predominant metamorphic basement. The rivers show a braided river pattern and are characterized by coarse sediment load. The High Rhine, which is a product of the confluence of the Hinterrhein and Vorderrhein, flows through a landscape predominantly consisting of Mesozoic limestone (Preusser, 2008).

Reaching the city of Basel, the landscape surrounding the river Rhine changes drastically. The part of the catchment from Basel to Mainz is characterized by Paleozoic sediments. From the city of Basel the Rhine enters the Upper Rhine Graben, which is part of the European Cenozoic Rift System (Preusser, 2008; Tockner et al., 2009). Because the Rhine has incised itself into the Graben, geological units in this area shift from the Mesozoic granite in the Graben to limestone from the Upper Eocene to fluvial deposits of the Rhine system of middle Pleistocene age at the margin of the Mainz Basin (Preusser, 2008; Tockner et al., 2009). The major tributaries are the Neckar and Main in this part of the catchment. These tributaries flow east of the Rhine Graben where the landscape mainly consists of pre-Permian granite. After the Rhine leaves the Mainz Basin, the river enters the Rhenish Massif and again cuts deeply into the Paleozoic basement. Passing through the Rhenish Massif, the Rhine confluences with the tributaries Lahn and Mosel, which flow through Lower Devonian shale and sandstone deposits.

When the Rhine leaves the Rhenish Massif, the downstream part of the Rhine catchment begins, consisting of the Lower Rhine and Rhine Delta. Tertiary and Quaternary sediments are well exposed in the Lower Rhine Embayment. Therefore, the area is very well known for the mining of coal. The change from Lower Rhine to the Rhine Delta almost coincides with the border between Germany and the Netherlands, where the Rhine splits into the Waal, Nederrijn-Lek and IJssel. The Waal and Nederrijn-Lek

continue to flow to western direction and form a broad delta with the Meuse River, whereas the IJssel flows in a northern direction. Predominant geological units are aging from the Pleistocene to Holocene in upwards direction and were repeatedly interrupted by marine influences (Preusser, 2008).

2.3 Climate and Hydrology

The general climate of the Rhine basin is characterized by a temperate climate zone with frequent weather changes. However, the climate changes from maritime to more continental from the sea to the east and southeast. Weather conditions during winter are primarily influenced by dynamics of the atmosphere in the Northern and Eastern Atlantic and the North Sea. With altitude, the temperature and precipitation changes considerably. Precipitation in the basin is on average 945 mm/year but due to the orographic effect of mountain ranges the precipitation can be significantly higher: the annual average precipitation lies around the 1500 to 2000 mm/year in the Upper basin (Tockner et al., 2009).

The annual discharge of the Rhine entering the Netherlands at Lobith is 2395 m³/s (Hartmann et al., 2007; Hurkmans et al., 2008)(Figure 3). This discharge is distributed over three distributaries, the Waal, Nederrijn-Lek and IJssel, which receive 65, 23 and 12% of the total discharge at Lobith respectively (Ten Brink, 2005). Furthermore, the main characteristics of the tributaries of the Rhine are shown in Figure 3. The Lower Rhine and Delta Rhine display moderate seasonal variation in the long-term mean monthly discharge. This is due to the fact that the annual flow pulse from the Alps, which is primarily fed by snow melt, arrives downstream when in the lower catchment the water budget is negative. Therefore, the hydrograph of the Alpine Rhine (Aare) will show a peak discharge during summer whereas the hydrograph at a location in the Lower Rhine (Mosel) shows a large peak discharge in winter, since the Rhine is fed by melt water in summer and rain-fed during winter (Tockner et al., 2009)(Figure 2). Most global circulation models show higher precipitation rates in winter and lower precipitation rates in summer for the Rhine Basin. This results in a shift in the seasonal pattern of the Rhine from a rain-fed/melt water-fed river into mainly rain-fed river (Pfister et al., 2004). Due to this shift, the hydrograph of the Rhine from the Middle Rhine to the sea will show a different pattern. It is expected that during winter the discharge will increase by 30% and during summer the discharge will decrease with 40% (Lenderink et al., 2007) due to the changing precipitation pattern.

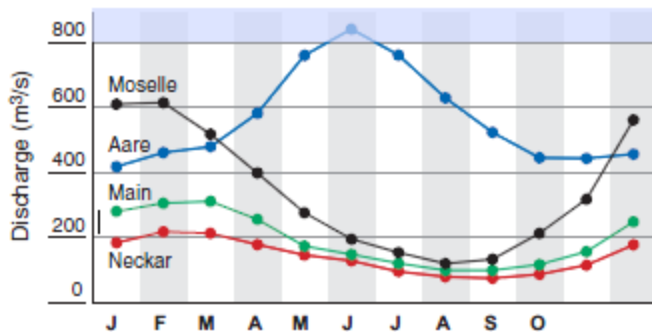


Figure 2: Average monthly discharge of the Rhine tributaries Aare, Neckar, Main and Mosel (Tockner et al., 2009).

Tributary	Gauge	Area, km ²	Mean Q, m ³ s ⁻¹	Max Q, m ³ s ⁻¹	MAM Q, m ³ s ⁻¹
Lahn	Kalkofen	5.304	48	587	394
Main	Raunheim	24.764	187	1991	1177
Mosel	Cochem	27.088	364	4009	2650
Neckar	Rockenau	12.710	154	2105	1396
Ruhr	Hattingen	4.118	75	867	611
Rhine	Lobith	185.000	2395	11775	8340

Figure 3: Tributaries of the Rhine Basin and their characteristics. The mean, maximum and mean annual maximum discharge (MAM Q) are calculated over the period 1993-2003 (Hurkmans et al., 2008)

The channel dynamics of the Rhine and its tributaries were dominantly climatically driven until the beginning of the 19th century. While sedimentation in the catchment increased drastically as a result of land use change, the river form remained largely unchanged. Prior to the 19th century the Rhine was a multi-channel river that braided upstream and meandered freely downstream with no human alterations to the flow path. However, the first intensive redesign of the Rhine took place during the 19th century during which the channel was simplified and straightened. Later the Rhine was channelized at multiple locations. These anthropogenic alterations changed the fluvial regime of the Rhine drastically (Pinter et al., 2006). Furthermore, due to engineering work to permit the passage of large ships, hydro-electric power plants and flood protection the channel dynamics changed excessively (Lang et al., 2003).

2.4 Geochemistry

Water and sediment chemistry along the Rhine reflects the modification of watershed characteristics (e.g. geology and vegetation), atmospheric input, anthropogenic sources and runoff patterns. The geochemical background of the catchment is of large importance to the chemical composition of the Rhine. Concentrations of major ions distinctly increase between the Alps and Rhine Delta (Tockner et al., 2009). The chemical content of the Rhine is monitored by the Dutch Ministry of Infrastructure and Water Management (Rijkswaterstaat). Water quality data obtained by Rijkswaterstaat over the period 1999 till 2007 showed that the ten most abundant trace metals in the surface water of the Rhine are Boron (B), Bismuth (Bi), Scandium (Sc), Barium (Ba), Lithium (Li), Sr, Ti, Mn, Zn and Rb (Figure 4)(Schrap, 2007).

The measured dissolved concentrations of the trace metals present in the river water after filtration of the sample through a 0.45 µm membrane filter can be observed in Figure 5. From this figure it can be observed that many trace metals are not measured although they were present in the total sample.. This means that many metals are only present attached to the suspended sediment or the metals are present as an insoluble complex or molecule. For example, the elements Pb and Tin (Sn) are measurable after filtration however, there is less than 10 % of the element concentration measured in the non-filtrated water sample. Thus, Pb and Sn are metals that are mainly present attached to particles or as insoluble complex. This effect causes a change in the abundance of trace metal concentrations in the Rhine. The most abundant trace metals in the dissolved phase are: Sr, B, Mn, Ba, Li, Selenium (Se), Rb, Ti, Zn, and Cu (Schrap, 2007).

The trace metal concentration and composition changed a lot as a result of human influences on the surface water of the Rhine. Especially Cr, Ni, Cu, Zn, Cd, and Pb are metals which became enriched mainly as a result of anthropogenic activities (Förstner & Müller, 1981). The human impact on the catchment increased drastically since the development of the coal and iron industry, the chemical industry and rapid urbanization along the Rhine and its tributaries. Some efforts were done to minimalize the impact; however these efforts could not keep pace with the fast increase of the growing wastewater production. Moreover, the government was reluctant to restrain the waste water production by the industrial sector, in order to obstruct the industrial growth. Until the 1970s water quality continued to degrade and it even became increasingly difficult to extract drinking water from the Rhine due to the high pollution rate of the water (Tockner et al., 2009). Until 1976, pollution of the Rhine by chemical wastewater was allowed. The International Commission for the Protection of the Rhine (ICPR) set up an action program in order to reduce the concentration of pollutants and restore the rivers

original flora and fauna. As a result harmful substances were cut by 70-100% and heavy metals were significantly reduced. An example: Recycling of industrial waste water and solid wastes by the metal industry. This reduced emissions of Cd, Pb and Zn alone with 14, 30 and 30% respectively (Stigliani et al., 1993). Within a period of 30 years the water quality of the Rhine experienced a serious improvement (Tockner et al., 2009). However, soil quality has not improved and predicted to worsen by Stigliani et al. (1993). Furthermore, considerable amounts of heavy metals have accumulated in the overbank sediments of the embanked floodplains (Middelkoop, 2000). The residence time of heavy metals in soils is larger than in air or water, resulting in a longer period of pollution in overbank and channel deposits.

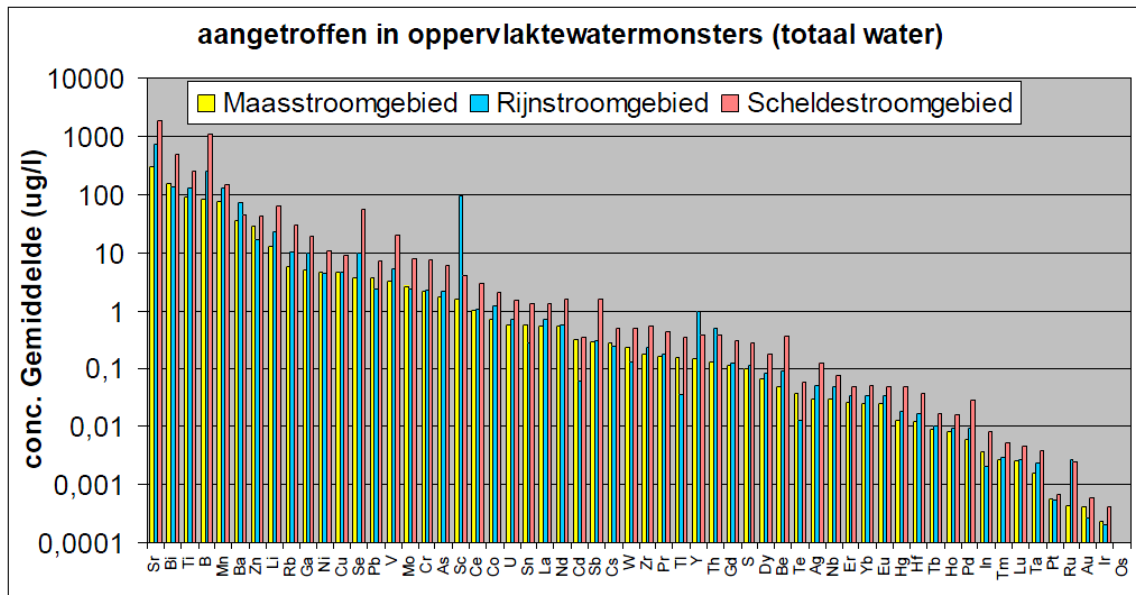


Figure 4: Total trace metal concentrations measured without filtrating the sample in the river Rhine shown in blue (Schrap, 2007).

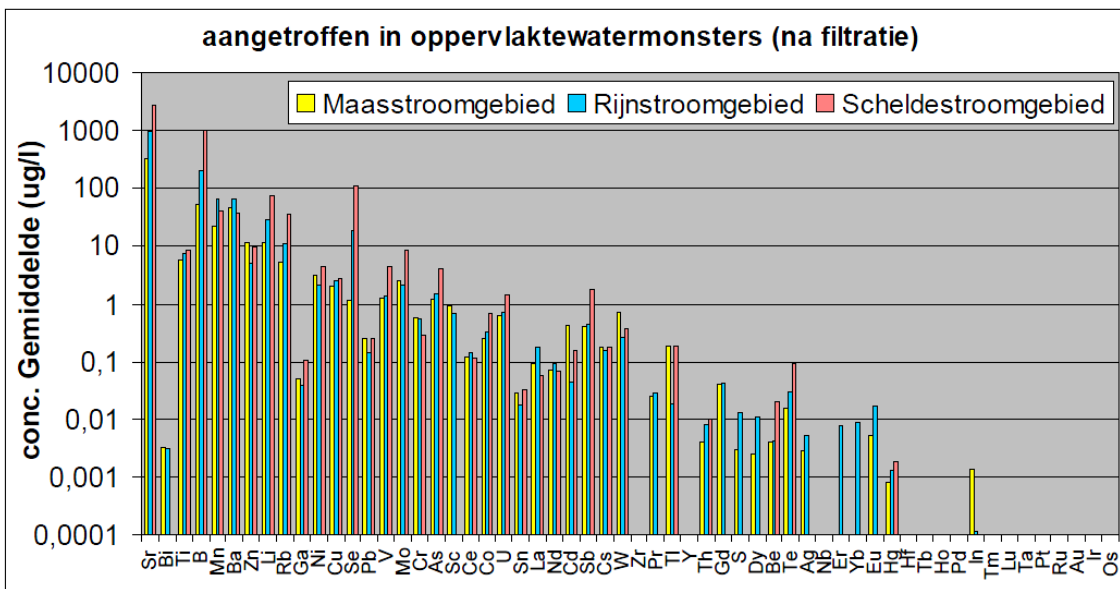


Figure 5: Dissolved trace metal concentration river Rhine shown in blue (Schrap, 2007).

3 Materials and Methods

3.1 Field sampling

3.1.1 Fieldwork Waal and Lek (Netherlands)

The main fieldwork campaign was conducted in the downstream part of the River Rhine in the Netherlands to collect suspended sediment samples. Criteria for the fieldwork were (1) a sufficiently short timespan in which sampling is carried out, (2) a sufficient mass of sediment, and (3) a sampling technique that is not labour intensive or expensive. Therefore, two kind of sample techniques were chosen, a time-integrated and a synoptic sampling technique.

Time-integrated suspended sediment sampling

For the time-integrated sampling technique, the Phillips Sampler developed by Phillips et al. (2000) satisfied all the criteria for sampling suspended sediment in the Rhine. In Figure 6 a cross-section of the Phillips sampler is shown. Along the river, the time-integrated samplers were installed, to collect the fine suspended sediment from the flowing water (Phillips et al., 2000).

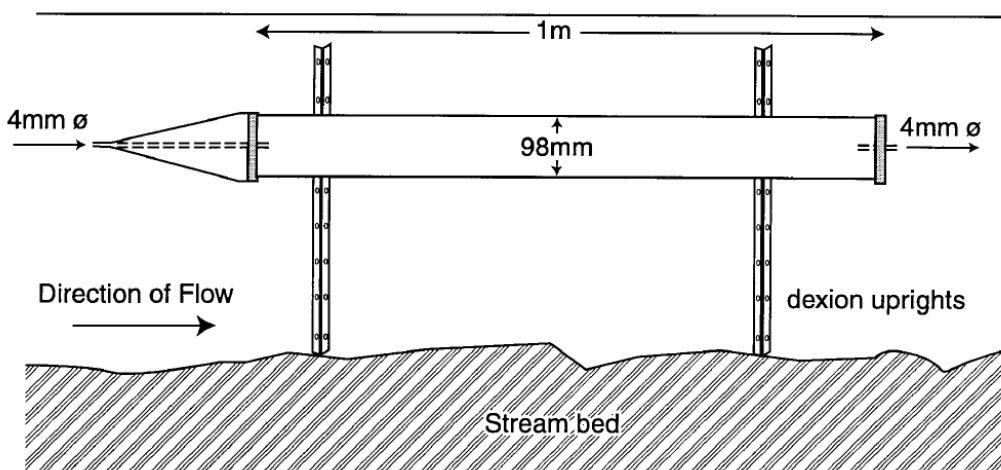


Figure 6: Cross-section of time-integrated suspended sediment sampler (Phillips Sampler) (Phillips et al., 2000).

During installation, the sampler was filled with local water after which the sampler was submerged in the channel at an average depth of 25 cm below the water level. The sampler was installed horizontally to the stream bed with the inlet in the flow direction. The Phillips samplers were mostly installed between groynes, where the flow direction was opposite of the flow direction in the channel. The sampler was attached to two steel uprights which were anchored in the channel bed. When the sediment sampler was installed, water entered the inlet tube continuously at a velocity proportional to the ambient flow velocity (Phillips et al., 2000). Within the main cylinder of the sampler, the flow velocity will reduce due to the greater cross-sectional area of the main cylinder compared to the inlet tube. As a result of the reduction in flow velocity, sedimentation of the suspended material occurred. The Phillips samplers were installed along the river Waal and Lek (Figure 7) and after approximately four weeks the obtained suspended sediment was collected and further analyzed in the lab.

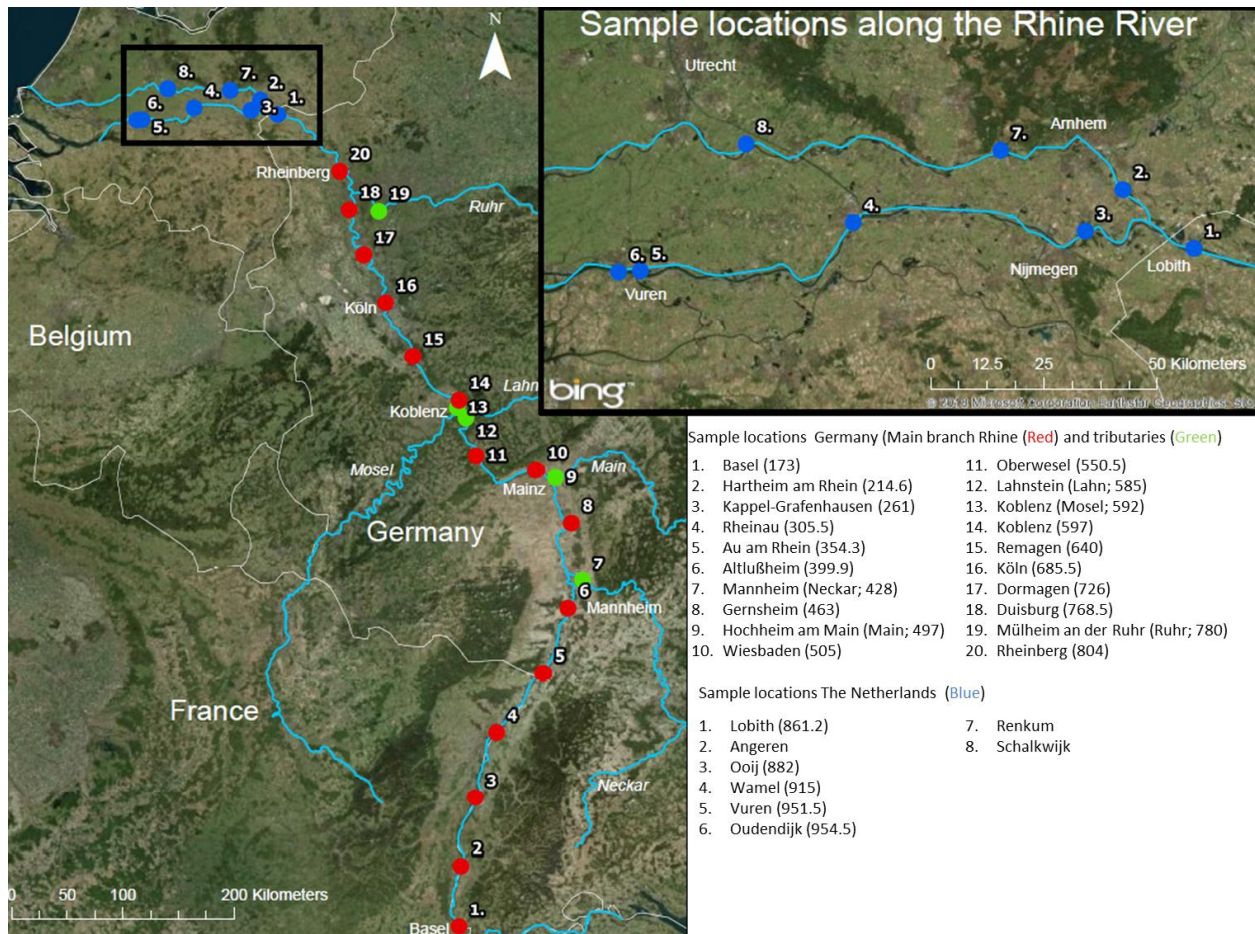


Figure 7: Sample locations along the Rhine River. Names of the sample locations in the Dutch (Blue) and German (Red and Green) corresponding Rhine-km are stated in the table (Geoportal Baden-Württemberg 2017; Geoportal Nordrhein-Westfalen, 2017; Geoportal Rheinland-Pfalz, 2017; PDOK, 2017).

Synoptic sampling of suspended sediment

For the synoptic sampling techniques, water samples and bed sediment samples were collected along the Rhine. The locations at which the water samples were obtained correspond with the installation locations of the time-integrated suspended sediment samplers. The water samples were obtained by filling two times a 1-liter bottle with channel water, using a stick with a bottle attached to it. The water samples were mainly extracted during normal water levels in the river. To get more insight in concentration variability of trace metals during high water levels, two sampling days were carried out during high water conditions in the Rhine. Moreover, to determine the variability within sample sets of the synoptic samples, 18 liters of water was collected at Vuren. Bed sediment was collected at Vuren and Schalkwijk to validate the concentrations measured after correction with the correction factor.

3.1.2 Fieldwork Germany

An additional fieldwork campaign was carried out in the German part of the Rhine river. During this campaign water and sediment samples were obtained at 20 locations (Figure 7) along the river starting from Basel. The water samples were obtained by a sample bottle attached to a stick, which made it

easier to collect suspended sediment from the channel. At each sample location 3 liter of water was collected for further analysis in the lab. Furthermore, 5 kg of bed sediment was collected at each sample location.

3.2 Laboratory analysis

3.2.1 Water samples

To retrieve the suspended sediment from the river water samples, the samples were filtrated. For the filtrating process membrane filters with a porosity of 45 μm and a diameter of 50 mm were used. To be sure no soluble substances are present in the filter originating from the production process of the filters, the filters were rinsed with distilled water before filtering the river water sample. Then the filters were dried in an oven at 70 degrees Celsius for four hours. When the filters were dry, the weight of each filter was measured. After this process, the river water samples were filtrated using the preprocessed filters.

For each sample location along the Rhine, 2 (the Netherlands) or 3 (Germany) liters of river water were collected in bottles. The volume of water that was filtrated was carefully measured. To obtain concise values when the filters were scanned by the handheld XRF, a substantial amount of sediment ($> 0.1\text{g}$) needed to be present on the filter. The filters with the obtained suspended sediment were put back in the oven at 70 degrees Celsius. When the filters were dry, the weight was measured again, and the weight of the sediment on the filter was determined by subtracting the initial weight of the filter.

3.2.2 Bed sediment samples

Variation of synoptic river water samples

Sediment collected at Schalkwijk and Vuren was used to assess the possible errors during the filtrating process of the water samples and for calculating the correction coefficient. The sediment was prepared in two different ways. Firstly, all sediment collected at the two locations was dried in an oven at 70 degrees Celsius. When the sediment was dry, it was either put in a sample cup to determine the bulk concentration of the sample or it was resuspended to get a synthetic sample with a known concentration that is representative for the downstream part of the river Rhine.

During random filtration experiments a synthetic suspended sediment sample was created by mixing 2 grams of the sediment sample obtained at Schalkwijk in 3 liters distilled water. This step was repeated four times to make four replicate samples with the same concentration. From this sample, different volume amounts were filtrated. First, the suspended sediment was filtrated 14 times with increasing volumes of the synthetic sample between 25 ml and 250 ml. Second, the suspended sediment was filtrated 14 times with decreasing volumes of the synthetic sample between 25 ml and 250 ml. Third, the suspended sediment was filtrated 14 times with random volumes of the synthetic sample between 25 ml and 250 ml. The fourth synthetic sample was prepared with sediment collected at Vuren, again putting random volumes of the sample on the filters ranging between 25 and 250 ml. The purpose of adding random volumes was to get homogeneous sediment samples. All filters used for the four methods were dried in the oven at 70 degrees Celsius after which they were analysed with the handheld XRF.

Wet sieving

To get insight in the relation between the trace metal concentrations in the suspended sediment and trace metal concentrations in the bed sediment, samples along the German part of the Rhine were collected. The collected sediment was too coarse for analyses and could cause an underestimation of certain concentrations. Therefore, sediment was sieved to obtain only the fraction smaller than 63 μm by wet sieving. The sediment was put in a sieve with a diameter of 63 μm and by adding distilled water the fine sediment was brushed through the sieve. The fine-grained sediment obtained by wet sieving was collected in a measuring cylinder of 1 liter. The settling velocity of the sediment in the cylinder was calculated using Stokes' law (Equation 1):

$$v = \frac{2}{9} * g * \frac{\rho_P - \rho_F}{\eta} * r^2 \quad (1)$$

Where v is the settling velocity of the particle in m/s , g is the acceleration due to gravity in m/s^2 , ρ_P is the density of the particle in m^3/kg , ρ_F is the density of the fluid in m^3/kg , η is the coefficient of viscosity of the fluid and r is the radius of the particle in m . Taking $\rho_P=1250 \text{ m}^3/\text{kg}$, $\rho_F= 1000 \text{ m}^3/\text{kg}$, $\eta=1.307$ and $r=3.15\mu\text{m}$, resulted in a settling velocity of $4.14 * 10^{-7} \text{ m/s}$. Considering the height of the cylinder was 0.4 m, it takes 11 days for all sediment to precipitate to the bottom of the cylinder. In order to enhance this process, 1 ml of a 1 Molar sodium chlorite solution was added. By adding this sodium chlorite solution, the distance between ions declined, resulting in more molecular collisions and thus flocculation. The radius of the particles become larger and thus the settling velocity increases. When sufficient amounts of sediment were present in the cylinder, the clean water was subtracted from the cylinder. Some sediment samples contain significantly less fine sediment than other sediment samples. To get enough fine sediment and get an accurate measurement, these samples should be sieved multiple times. The sediment was put in oven trays and then put in the oven at 70 degrees Celsius to evaporate the water from the sediment. It took around 24 to 36 hours to evaporate all the water from the sediment. The dried sediment was placed in the sample cups with a volume of 10.6 cm^3 for further XRF analysis.

3.2.3 Phillips samplers

The collected sediment obtained by the time-integrated suspended sediment samplers was stored for a couple of days in the sample bottle, in order to settle all obtained sediment. When all sediment was settled, the overlying water was decanted. The sediment was put into the oven at 70 degrees Celsius to dry. When the sediment was dry it was put in sample cups with a volume of 10.6 cm^3 and the sediment was ready to be analyzed with the handheld XRF.

3.3 Data analysis

3.3.1 Validation of the used methods

Correction parameter

The XRF measurement of a soil or sediment sample requires a minimum thickness of about 5 mm of sample. Because the small amount of sediment on the filters, this minimum requirement is not met and, as a consequence, the XRF analyzer gives a lower concentration than the actual concentration in the

suspended sediment. The XRF signal or measured concentration had to be corrected for this effect. For this, the following power function was used:

$$y = a + ab^x \quad (2)$$

Where y is the measured concentration with the handheld XRF in ppm, a is the actual concentration in ppm, b is the correction parameter and x is the weight of the sediment that is present on the filter in g. The correction parameter for each element was calculated using the measured concentrations of the random filter series of sediment samples obtained at Vuren and Schalkwijk. As a reference, the same sediment was put in sample cups and the concentration was measured to obtain the actual concentration. The geometric mean was taken for all calculated correction parameters of both sample series. The geometric mean was used, since the calculated correction parameters had different numeric ranges. This made it possible to take an average of the correction parameter in which no range dominates the weighting. To check if the eventual calculated correction parameter provided a reasonable actual concentration, the actual concentration was compared to the average concentration of the sediment cups of sediment samples obtained at Vuren and Schalkwijk. The acceptability of the correction parameter was tested by producing a scatterplot with the weight of the sediment against the measured, corrected and reference concentration. The validated correction factor, which consists of the correction parameter (b) in combination with the sediment weight on the filter (x), was used for further analyses of the created data with the XRF.

Variation of synoptic suspended sample sets

The collected synoptic suspended sediment samples were filtered, so that the suspended material was separated from the river water. However, due to potential concentration differences during the collection of the river water, the concentrations of trace metals present in the sediment could be variable. Therefore, more insight was needed in the variation of trace metal concentrations in the suspended sediment between the taken samples and within the sample set. By variation within a sample set is meant the variation between the measured concentrations of one filter, since each filter is measured three times with the XRF scanner. To study these variations between and within the taken samples, 18 Liters of water was collected at Vuren. On every used filter, 1.5 Liters of water was filtrated so that in the best case scenario, the weight of the sediment trapped on each filter was equal. With the best case scenario it is assumed that since the water samples are taken at the same time and location, the samples are equal resulting in the same sediment weight on the filter. When the sediment on the filter was dry, concentrations of the present elements were measured with the handheld XRF. Each filter was scanned three times to correct for unequal distribution of sediment on the filter. The variation of the actual concentration of each measurable trace metal was investigated by first correcting the measured concentration. Then the weight of the sediment present on the filter was plotted against the corrected concentration for each measured element. This resulted in an overview graph per element which represents the variation per taken water sample. Furthermore, the variation of the concentrations within a sample set could be determined since each filter was scanned three times.

Comparison of synoptic sediment concentrations with time integrated sediment concentrations

The concentrations measured in the synoptic suspended sediment samples that were taken at each location along the Rhine were corrected since the amount of suspended sediment that is measured using this technique is small. To get more insight in the precision of the synoptic sampling method, the concentrations measured from the synoptic river water samples were compared with the measured concentrations in the suspended sediment using the time-integrated sampler. Suspended sediment from the time-integrated Phillips sampler was collected during sample dates 28-09-2017 and 19-10-2017. During these sample dates, synoptic samples were collected as well. The concentrations of the suspended sediment from both sampling techniques were plotted against sample location for each element.

Wet sieving

Bed sediment that was collected during the sampling campaign in Germany was measured as a bulk sediment sample and a sample with only the sediment fraction smaller than 63 μm . To determine which method was most suitable to compare the trace metal concentrations of suspended sediment with trace metal concentrations the bed sediment, the concentrations were plotted against sample locations for each measured element. This made it possible to determine if the sediment should be sieved in order to observe patterns or trends in the spatial distribution and variation of the chemical content of the bed sediment and to compare the possible variation with the suspended sediment obtained at the same location. Since suspended sediment has a fraction smaller than 63 μm , it was expected that the sieved sediment samples show better results than the bulk sediment samples, as sediment that show no characteristics of suspended sediment were not measured.

Comparison with existing data

To verify the measured concentrations for both the synoptic and time-integrated suspended sediment samples, the actual concentrations that were obtained during the field campaign in the Netherlands were compared with data measured by the Dutch Ministry of Infrastructure and Water Management (Rijkswaterstaat). The data that was collected by Rijkswaterstaat consists of the long-term yearly variation of the concentration of trace metals transported through the river channel. Therefore, the obtained concentrations of this study are easily compared with the long-term average. The concentrations were measured at Lobith and Vuren between 1988 till 2016. Even though some elements were measured during a shorter time period, a good comparison can be made between the different concentrations and trace metals. The element concentrations measured in suspended sediment samples obtained with both techniques and the concentrations measured by Rijkswaterstaat were plotted against time.

3.3.2 Spatial and temporal variation of the chemical composition of suspended sediment

General variation

After the concentrations of the trace metals were measured with the handheld XRF and the used sampling methods were validated, the spatial and temporal variation was investigated. The overall variation, temporal and spatial, was studied by calculating Pearson's correlation coefficient between the

measured elements at each sample location and between the element concentrations with changing water height. This could indicate relations between elements with the same type of temporal or spatial variation through the system. Values of the calculated correlation coefficient range between the -1 and 1. Positive correlation indicates that both variables increase (1) or decrease together, whereas negative correlation (-1) indicates that one variable increases and the other decreases. First, the correlation coefficient was calculated between all elements measured on every sample location along the Dutch Rhine. Then, the correlation coefficients between all elements were calculated per sample location. As a result, the relationship between the elements could be analyzed between the different sample locations and between the overall relation of the elements and changes of the correlation coefficient could easily be detected.

Temporal variation of the chemical composition of suspended sediment

The temporal variation of the chemical composition of the Rhine was determined with the collected synoptic and time-integrated suspended sediment samples that were taken along the Dutch part of the Rhine. The concentrations measured in the synoptic sediment samples were corrected. After correction all concentrations were plotted against sample date. This was performed for each element in order to get more insight in the concentration variation over time per measured element. It was expected that the water level in the Rhine had a major effect on the concentrations that are present in the suspended sediment. Therefore, the water level, measured by Rijkswaterstaat, was plotted in the same graph. This made it possible to compare the temporal variation of each measured element in the suspended sediment with changing water height. Furthermore, the color of the sediment can indicate the chemical and organic content of sediment. Kononova (1961) stated that the color of sediment becomes darker with a higher concentration of organic matter and this was used to determine organic matter content in soil formations. In order to get an objective scale of colors, the Munsell color chart was used (Munsell & Nickerson, 1940). In this chart, colors are ordered in terms of Hue, Chroma and Value which are represented as H, C and V respectively. These values were used to study the relation between the concentration variation in suspended sediment and the color of the sediment.

Spatial variation of the chemical composition of suspended sediment

The Netherlands

The spatial variation of the chemical composition of the Rhine was determined with the collected synoptic and time-integrated sediment samples that were taken along the Dutch part of the Rhine. The concentrations measured in the synoptic sediment samples were corrected. After correction all measured concentrations were plotted against sample location. This was performed for each element to identify the variation of the concentrations more clearly. Furthermore, the sample locations are represented in Rhine-km. The Rhine-km is a unit in which the locations along the Rhine are specified in order of length, counted from the source which was defined by the International Commission for the Hydrology of the Rhine basin (CHR) (CHR, 2015). Figure 7 shows the sample locations with corresponding Rhine-km.

Germany

To investigate the spatial variation in the German reach of the Rhine, the concentrations of the trace metals of the suspended sediment and bed sediment were analyzed. Again all concentrations measured using the synoptic method were corrected. Then, the concentrations of the trace elements in the suspended sediment of the main branch of the river Rhine were plotted against the sample locations in Rhine-km. The concentrations of the main Rhine branch and the concentrations of the tributaries are divided in the graph. This made it possible to compare the concentrations flowing through the main branch with the concentrations that were originating from tributaries and therefore clarify for possible changes after the inflow of the tributary in the main branch. For the bed sediment, the bulk sediment and the wet sieved were analyzed with the handheld XRF. The concentrations of both kinds of samples do not need to be corrected for. The concentrations were plotted against the locations in Rhine-km. As a result, the concentrations of sieved sediment samples could be compared with the bulk sediment and concentrations of sediment of the tributaries could be compared with the sediment obtained from the main branch of the Rhine.

4 Results and Discussion

4.1 Validation of the used methods

4.1.1 Correction parameter

To correct the measured element concentrations in the synoptic sediment samples, the correction parameter was validated. In Table 1 correction parameters of all measured elements in the suspended sediment are shown. The correction parameter increases with increasing atomic number of the element. This means that elements with a higher atomic weight needed more correction to get a comparable concentration to the reference sample. The correction factor, which consists of the correction parameter in combination with the sediment weight on the filter per sample, was used to estimate the actual concentration. In Figure 8, the measured and corrected Ti and Cr concentrations and the reference concentration obtained from the bulk sample were plotted against sediment weight on the filter. All other graphs for other measured element concentrations can be found in Appendix B.

In Figure 8 the measured concentration from the sediment on the filters can be compared with the reference concentration. With increasing sediment weight on the filter, the concentrations that are measured in the suspended sediment gets closer to the reference level. Therefore, the correction factor for filters with a smaller sediment weight should be corrected with a higher value. The correction factor consists of the correction parameter in Table 1 in combination with the sediment weight. The actual concentration approached the reference concentration measured in the bulk sediment closely. The corrected concentrations showed higher variation for samples with a low sediment weight than for samples with a high sediment weight. When the sediment weight on the filter exceeds 0.01 g, the precision of the approach of the corrected concentration to the reference concentration was the highest. To summarize, the overall precision of the correction factor that was used to calculate the actual concentration of the measured elements in the synoptic suspended sediment samples was high. The precision of the correction factor is the highest when the sediment weight on the filter exceeds 0.01 g.

Table 1: Measured trace metals with corresponding correction parameter (b).

Element	Correction Parameter (b)
Ca	9.30435E-05
Ti	5.85E-05
Cr	2.00048E-05
Mn	0.000689
Fe	0.009699
Cu	0.031919
Zn	0.032926
Rb	0.305539
Sr	0.4452
Zr	0.474553
Pb	0.235689

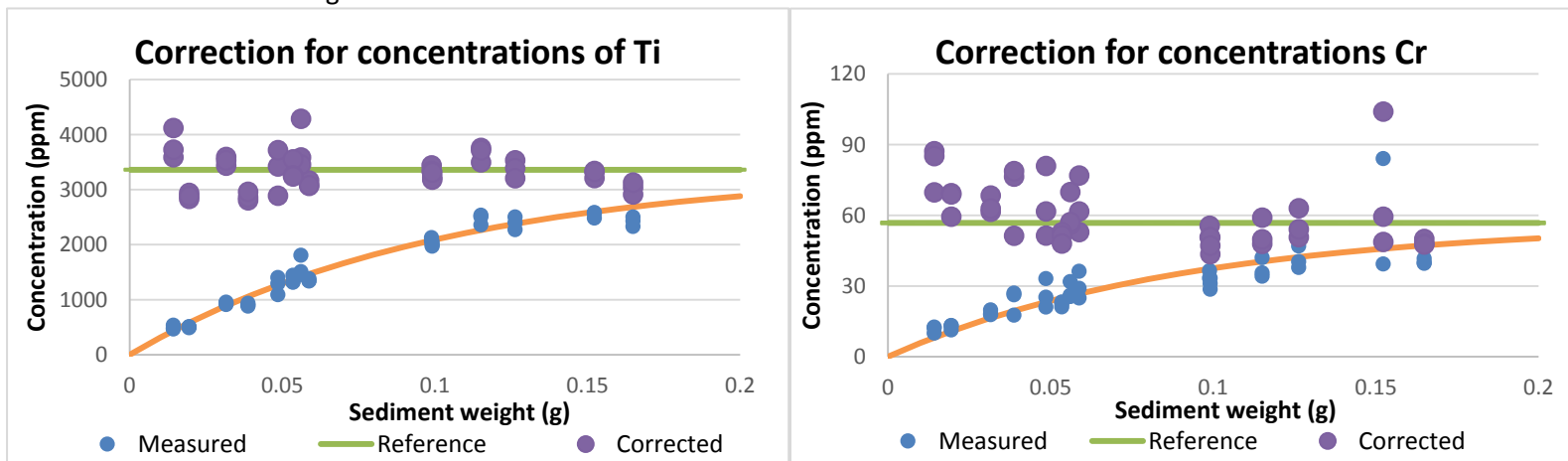


Figure 8: Validation of the correction parameter with concentrations of Ti.

4.1.2 Variation of synoptic suspended sample sets

The measured concentrations and average concentrations of a sample set from the synoptic sediment samples obtained at Vuren (section 3.3.1) were plotted against the sediment weight present on the filter (Figure 9). It can be observed that the variation of each measured element concentration was largest when sediment weight was smaller than 0.01 g. Moreover, the variation of the concentrations measured on the same sample filter was more prominent with sample filters containing less than 0.01 g of suspended sediment. The average concentration differed considerably compared to the minimum and maximum measured concentration within a sample set when the sediment weight on the filter was lower than 0.01 g. When the amount of sediment on the filter increased, the variation of the measured concentration of suspended sediment on the filter became less pronounced. The average measured concentrations of filters with more than 0.01 g of sediment on the filter were positioned closer to each other. This was valid for the variation of the concentrations measured on the same filter as well, since the variation of the concentration of the suspended sediment on the filter within a sample set became less when the sediment weight is greater than 0.01 g. This was valid for all measured elements in the sampled suspended sediment at Vuren.

From the graphs in Figure 9 it can be concluded that the variation of the concentrations within a sample set is largest when the sediment weight on the filter is less than 0.01 g, since the measured concentrations on the same filter differ greatly. Moreover, the variation between sample sets was high when the sediment weight was below 0.01 g, since the average of the measured concentrations in the suspended sediment were more scattered. This means that the precision of the synoptic sampling method was low when sediment weight on the sample filter did not reach 0.01 g. The precision was high when there was a sufficient amount of sediment on the filter. It can be concluded that the precision of the measurement of synoptic samples with the handheld XRF are highly dependent on the sediment weight on the filter and that the precision increases with increasing sediment weight.

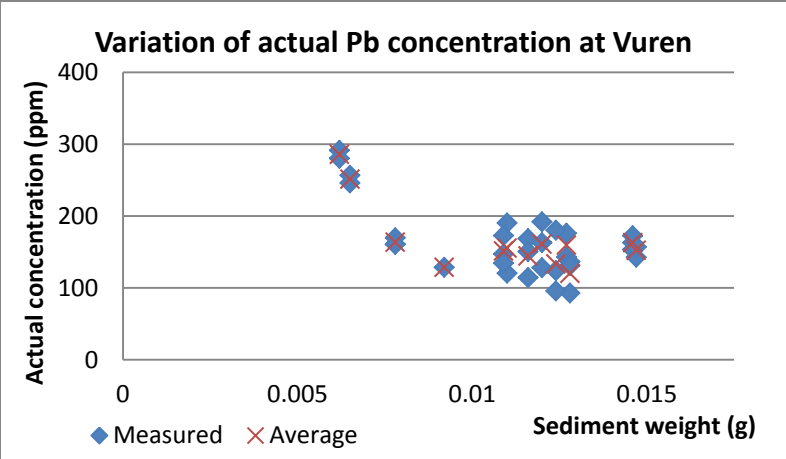
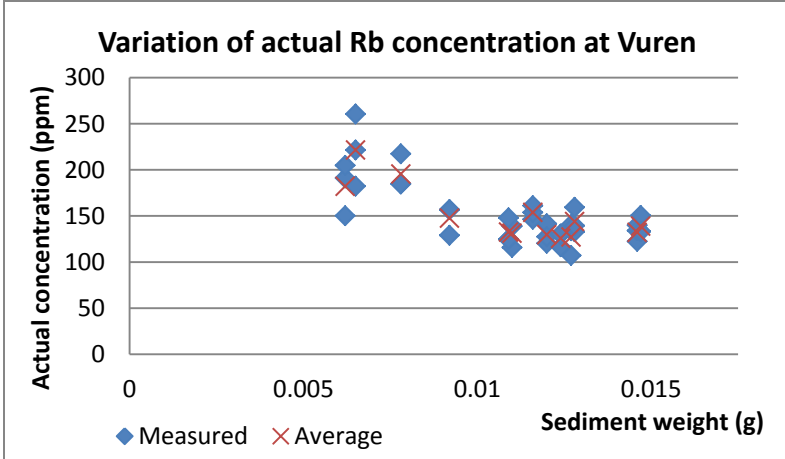
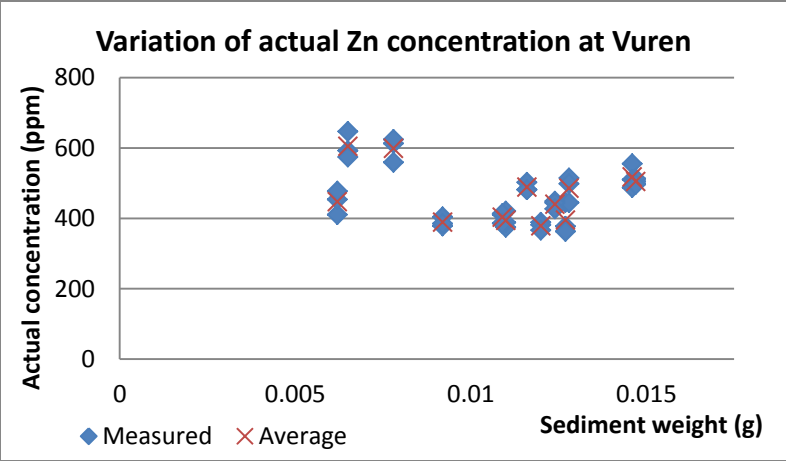
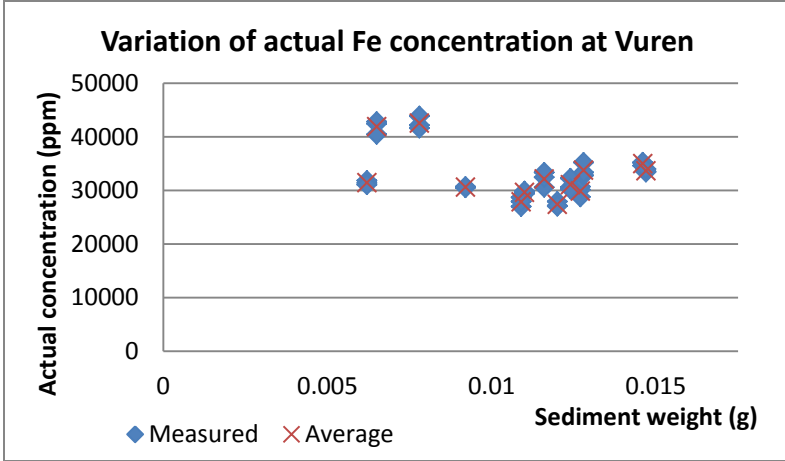
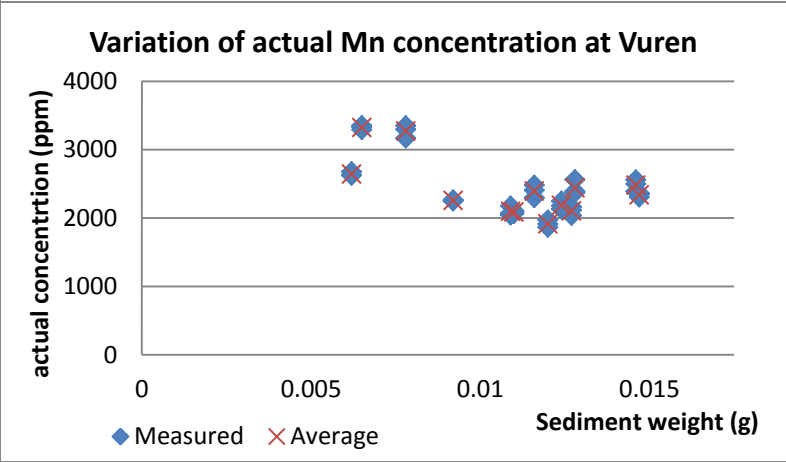
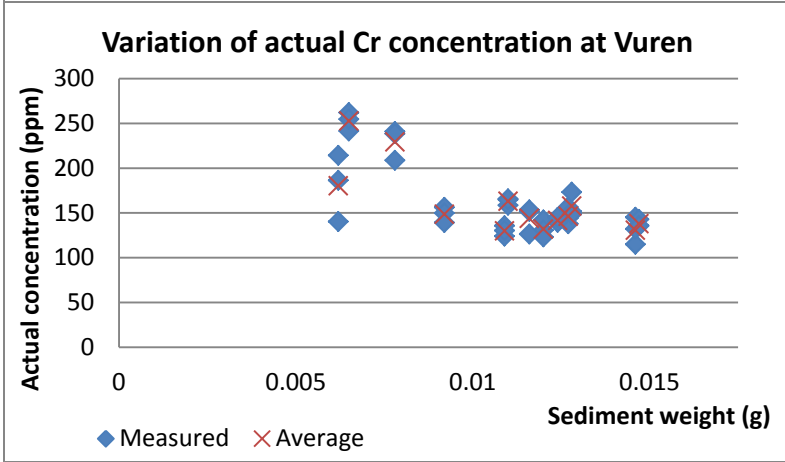
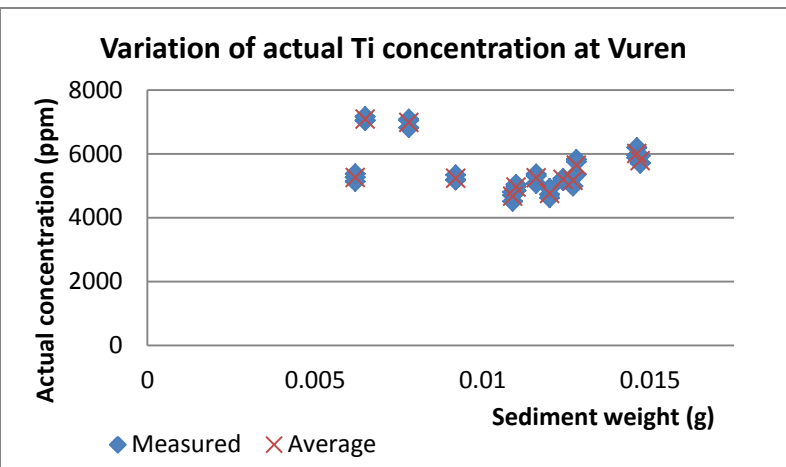
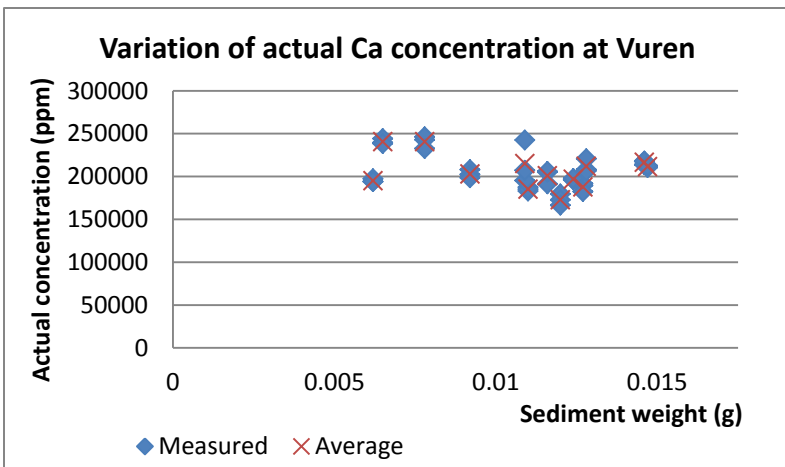


Figure 9: Variation within a sample set at Vuren of multiple concentrations of trace metals

4.1.3 Comparison of synoptic sediment concentrations with time integrated sediment concentrations

The concentrations of the synoptic sediment samples that were corrected with the derived correction factor needed to be verified. Therefore, the concentrations obtained from the synoptic and time-integrated sediment samples during sample dates 28-09-2017 and 19-10-2017 were compared. With the handheld XRF it is possible to detect more elements from the time-integrated suspended sediment than from the synoptic suspended sediment. Elements that are measured by the XRF in the time-integrated samples but that are not measured in the synoptic samples are Arsenic (As), Ba, Sn and Hg. Moreover, Molybdenum (Mo) and P were measured several times in the time-integrated sediment samples but not once measured in the synoptic sediment samples.

In Figure 10, Ti and Pb concentrations were plotted against sample location for both sample dates. Overall, the concentrations measured with the time-integrated Phillips Sampler showed similar values compared to the corrected concentrations from the synoptic suspended sediment samples. However, at sample location Ooij, the Ti concentrations measured with the time-integrated Phillips sampler were considerably lower during 19-11-2017. The lowered concentration for Ti at this location did not coincide with a lowered Pb concentration during the same sample date. The concentrations in the sediment obtained by both techniques showed the least concentration variation in the downstream part of the study area, around Vuren and Oudendijk. The average Ti and Pb concentrations measured for the water samples lie around the 3900 and 102 ppm respectively, whereas the average concentration measured with the Phillips sampler of both trace metals are approximately 3500 and 107 ppm respectively.

Since more sediment is collected by the time-integrated sample technique, more elements can be measured with the handheld XRF. The sediment amount that was present on the filter after filtration of the synoptic samples was not enough to measure the elements As, Ba, Sn and Hg. However, after correction was applied to the measured concentrations with the XRF, trace metal concentrations resembled concentrations measured in the time-integrated sediment. Because the samples were

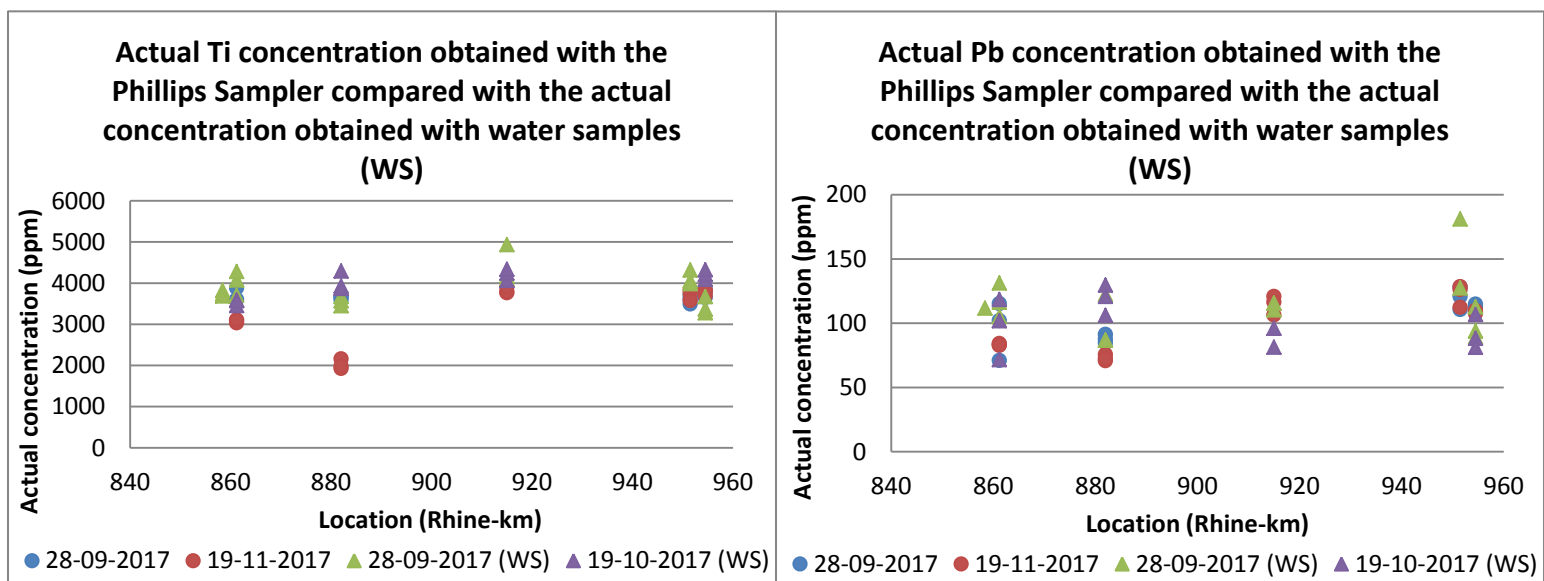


Figure 10: The actual concentration of Ti and Cr obtained with the time-integrated Phillips Sampler compared with the actual concentrations obtained by correcting the measured concentrations from the water samples.

measured three times by the handheld XRF, the uncertainty within the sample is accounted for. The concentration variation between the sediment samples obtained from the Phillips samples and water samples at Ooij are not visible within other trace metal concentration variations measured at this location and are thus unique for Ti.

4.1.4 Wet sieving bed sediment

The Zn concentrations measured in the bulk and sieved bed sediment obtained in the German reach of the Rhine were representative for all measured elements and are shown in Figure 11. In addition, the concentrations of all other measured metals in the bulk sediment can be found in Appendix C.

The concentration measured in the bulk sediment showed very low concentrations for Zn and other trace metals. The Zn concentration in the main branch of the Rhine was constant throughout the channel, with small variations between the sample locations and elevated concentrations between 450 and 600 km. The average measured Zn concentration in the bulk sediment of the main branch was 81 ppm with a maximum concentration of 246 ppm in the bed sediment of the main branch. However, the tributaries Lahn and Ruhr showed significantly higher Zn concentrations with an average of 1250 ppm.

The sieved sediment showed higher concentrations for the measured trace metals with respect to the measured concentrations in the bulk sediment. Moreover, the concentrations measured in the sieved sediment samples showed mostly an increase whereas this increase could not be measured in the bulk sediment. In the case of Zn, concentrations increase in the downstream direction from 162 ppm to a maximum of 1200 ppm. The highest concentrations were found between 600 and 800 km below the Rhine source. The concentrations measured in the tributaries Lahn and Ruhr in the sieved sediment were proportional to the concentrations obtained in the bulk sediment. However, the concentrations of trace metals in the tributaries Lahn and Ruhr were not as extreme as in the bulk sediment because concentrations in the main branch of the Rhine showed higher concentrations.

The results showed that only a good comparison can be made between the suspended sediment and the bed sediment, when the bed sediment was first sieved. The sieved sediment samples showed a better resolution of the spatial variability of the chemical composition of the bed sediment of the Rhine catchment. To summarize, the trend for each measured trace metal becomes more distinct when the sediment is firstly sieved before measuring with the handheld XRF. Therefore, the spatial distribution of the chemical composition of sediment in the German part of the Rhine will be studied by looking at the sieved sediment samples and comparing this to the synoptic suspended sediment samples.

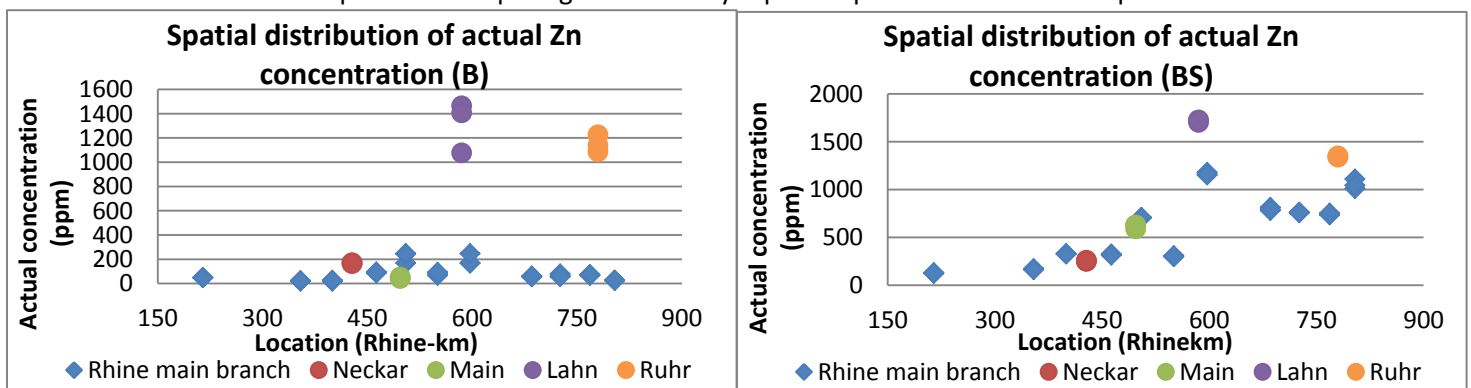


Figure 11: Spatial distribution of Zn concentration measured from the Bulk sediment (B) and sediment after wet sieving (BS)

4.1.5 Verification of measured chemical content of suspended sediment with data from Rijkswaterstaat

The concentrations measured by Rijkswaterstaat showed high variations. The concentrations of the elements Ca, Ti, Cr, Cu, Zn and Pb showed a slight decrease over time. Furthermore, the concentrations of the elements Ca and Pb showed seasonal variation patterns. As a result of the abundance of measurements and the long period of time that Rijkswaterstaat measured the concentrations of trace metals, the patterns of seasonal variability were harder to observe for the other elements. However, when zooming in on a shorter period, all elements show a form of seasonal variability. The concentrations of the trace metals that are measured in the synoptic sediment samples and time-integrated sediment samples during this study, showed a good resemblance with the long-term average concentrations measured by Rijkswaterstaat. Especially the concentrations for the metals Mn, Fe, Cu, Zn, Sr and Pb were comparable with the long-term average. However, the measured Ca, Cr and Rb concentrations measured in sediment samples from both sample techniques were considerably higher than the long-term average measured by Rijkswaterstaat. For Ti this was only the case when the concentrations were estimated from sediment collected by the time-integrated Phillips sampler.

From these results it can be concluded that the sampling methods, both the synoptic sediment samples and time-integrated Phillips samples, generated accurate and representative concentrations for the trace metals present in the chemical composition of suspended sediment in the Rhine. Although concentrations of Ca, Cr and Rb are overestimated for both kinds of sediment samples and Ti for the time-integrated sediment samples, all other elements showed values representative for the long-term average. In addition, the sampling methods that were used in this study had some great advantages compared to the method that was used by Rijkswaterstaat. For example, the concentrations obtained by Rijkswaterstaat were measured monthly. Since this is a large period with respect to concentration variations, small scale variations in the concentrations of the chemical composition of suspended sediment caused by flood events might be neglected. Therefore, a synoptic sampling technique was used in order to measure the trace metal concentrations in the river water more frequently. Moreover, installing time-integrated Phillips samplers on multiple locations along the Rhine will give a good indication of concentration fluctuations in both time and space.

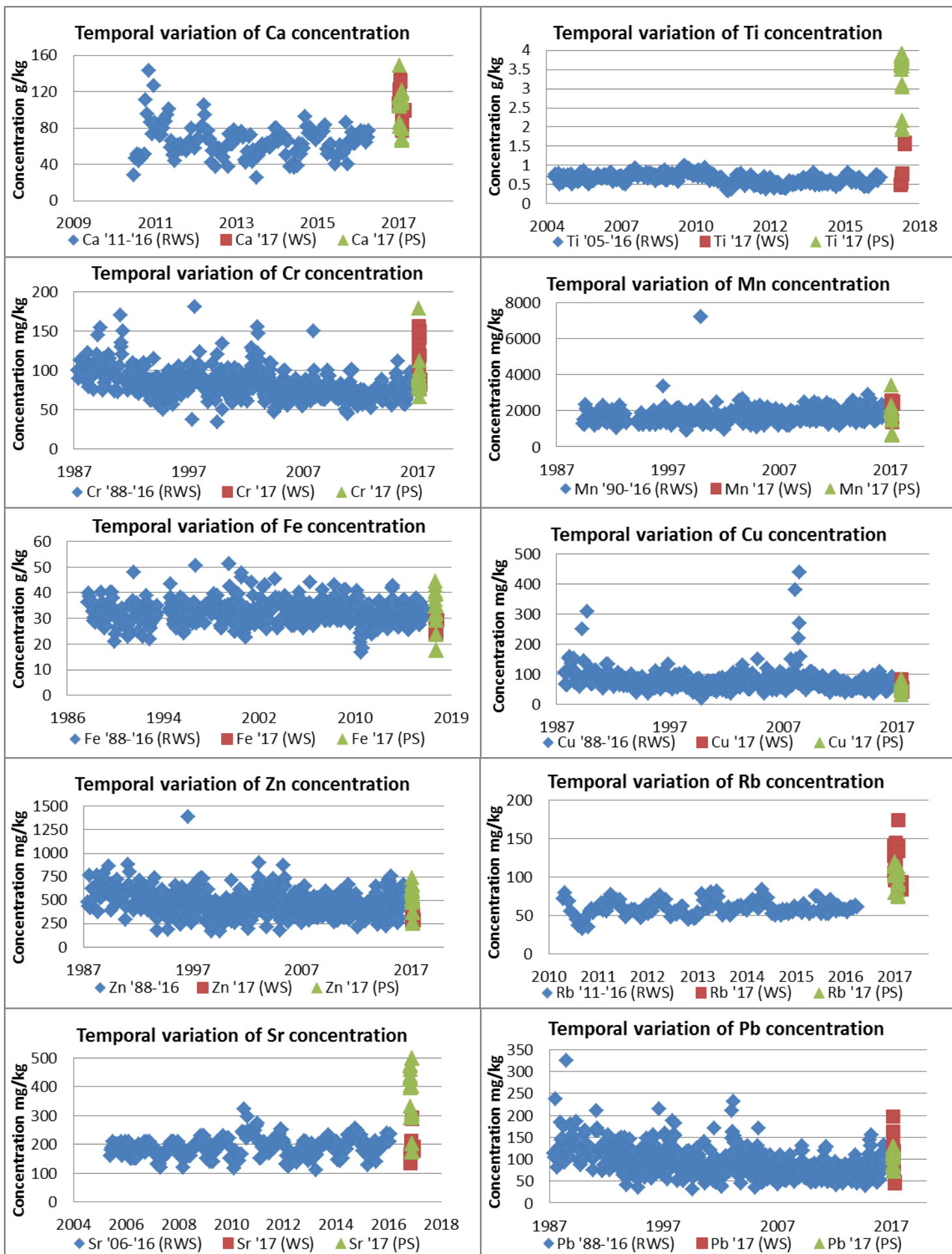


Figure 12: Verification of the measured concentrations of the synoptic suspended sediment samples (WS) and time-integrated suspended sediment samples (PS) for each element by comparing temporal variation of the measured concentrations with the concentrations measured by Rijkswaterstaat (RWS).

4.2 Temporal and spatial chemical variation of suspended sediment

4.2.1 General variation

The correlation coefficient was calculated between all the measured elements for all obtained data (Table 2) and at the sample location Lobith (Table 3). Moreover, the correlation coefficient between the measured concentrations and changing water height was calculated (Table 4). Measured correlation coefficients between the concentrations of elements measured at the remaining sample locations are presented in Appendix D.

The calculated correlation coefficients for all obtained concentrations along the Dutch part of the Rhine showed a high positive correlation (Red) between the elements Ca/Mn, Ti/Fe, Cr/Rb, Fe/Rb and Cu/Rb with coefficients varying between the 0.61 and 0.81. Calculated coefficients between Ca/Fe and Ca/Rb with values between -0.66 and -0.63 respectively, showed a high negative correlation (Blue). The calculated correlation coefficients between the concentrations measured at sample location Lobith showed a high positive correlation (Red) between Ca/Mn, Ca/Zn, Ti/Fe, Mn/Zn, Fe/Rb and Cu/Rb with coefficients varying between the 0.69 and 0.89. Correlation coefficients between the elements Ca/Fe, Ca/Rb, Mn/Fe, showed high negative correlation (Blue) with coefficients varying between -0.71 and -0.83. The calculated correlation coefficients between the measured concentrations and the water height in the river show a positive relation between the water height and elements Ti, Fe and Rb (Red). A negative relation can be identified between the water height and elements Ca, Mn, Zn and Cu (Blue). For the elements Sr, Cr and Pb no clear relation is present.

When the correlation coefficients calculated over the total measured concentrations were compared with the correlation coefficients of a single sample location (in this case Lobith), the relations that were strongest between elements remained the same. However, the relation at a single sample location showed stronger relations. For example, the relation between the elements Mn/Zn was not remarkable in the total concentration data, whereas the correlation coefficient between the concentrations measured at Lobith, Wamel and Oudendijk showed a more prominent relation between Mn/Zn. The same goes for the relation between Mn/Rb which kept a constant negative correlation until Oudendijk where the relation became unconsiderable. Moreover, element concentrations measured in suspended sediment showed two kind of relations with changing water height (Table 4). The relation between the measured elements in the suspended sediment and the water height was more prominent when measured concentrations for one single sample location were used.

The relations visible in Table 4 provided a subdivision into three categories of the measured elements. The elements Ti, Fe and Rb showed a positive correlation with changing water levels, meaning that the concentrations of these elements increased with increasing water level. The elements Ca, Mn, Zn and Cu showed a negative correlation with increasing water levels, meaning that the concentrations of these elements decreased with increasing water levels. Elements Sr, Cr and Pb did not show a clear reaction to changing water levels. These three categories are supported by the relations observed in Table 2 and 3. Here elements in the same category showed the strongest relations. For example, the elements Fe and Ti are both elements which showed increasing concentrations with increasing water level. Correlation

coefficients presented in Table 2 and 3 provided values of 0.8 for both the total data set and the measured data at Lobith.

However, there are exceptions in the categorization of elements based on the calculated relations. Boës et al. (2011) mentioned the strong relation between Ti and Rb and calculated the correlation coefficient with concentrations obtained from sediment cores. The study estimated the Pearson's correlation coefficient for Ti/Rb to be 0.85 which is significantly higher than the calculated value of 0.41 in this study. This lower correlation coefficient might be the result of the variation within the sample sets. For Rb the variation between samples in a sample set was larger than for the other elements. Moreover, the trace metal Cu showed strong relations with elements that showed opposite reactions with respect to the water level in the Rhine. This can be explained by the fact that Cu concentrations were not measured in the suspended sediment during high water levels. The reaction of the Cu concentration on high water was not taken into account, which caused a stable concentration variation.

Table 2: Correlation coefficients between the element concentrations for the total data set. Numbers in red show elements with high positive correlation, numbers in blue show elements with high negative correlation.

	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Rb	Sr
Ca	1								
Ti	-0.29474	1							
Cr	-0.4346	0.598742	1						
Mn	0.616506	0.012516	-0.34604	1					
Fe	-0.66076	0.814178	0.6618	-0.46555	1				
Cu	0.121193	-0.05989	0.507992	-0.25345	-0.21573	1			
Zn	0.598858	-0.13929	-0.21382	0.478998	-0.47382	0.431443	1		
Rb	-0.6357	0.559094	0.742693	-0.56369	0.808484	0.634978	-0.44141	1	
Sr	0.393241	0.124619	-0.15407	0.019089	0.10441	0.062157	0.295389	-0.00162	1
Pb	0.119953	0.151259	0.531868	-0.04837	0.07497	0.51956	0.44068	0.287034	0.208742

Table 3: Correlation coefficients between measured element concentrations at sample location Lobith, The Netherlands. Numbers in red show elements with high positive correlation, numbers in blue show elements with high negative correlation.

	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Rb	Sr
Ca	1								
Ti	-0.36274	1							
Cr	-0.04859	0.620901	1						
Mn	0.897542	-0.19113	-0.08756	1					
Fe	-0.8307	0.79345	0.380398	-0.71114	1				
Cu	-0.26478	-0.49848	0.103859	-0.68083	-0.52165	1			
Zn	0.797001	-0.45187	0.028098	0.730466	-0.8246	0.626325	1		
Rb	-0.71336	0.415408	0.339472	-0.78074	0.690583	0.858247	-0.44785	1	
Sr	-0.3687	-0.54361	-0.33633	-0.47769	-0.23365	0.637003	0.173477	0.562624	1
Pb	0.212748	-0.04358	0.61631	0.110513	-0.24978	0.652931	0.606665	0.106692	-0.14666

Table 4: Correlation coefficient between the measured concentrations and water height. Numbers in red show elements with high positive correlation, numbers in blue show elements with high negative correlation.

	Water height (total data)	Water Height (Lobith)
Ca	-0.78809	-0.88645
Ti	0.576538	0.710187
Cr	0.489612	0.265023
Mn	-0.61988	-0.72109
Fe	0.892091	0.972226
Cu	-0.5646	-0.7327
Zn	-0.62532	-0.86935
Rb	0.661445	0.604436
Sr	-0.09664	-0.26339
Pb	-0.13781	-0.2853

4.2.2 Temporal chemical variation of suspended sediment in the Rhine

Figure 14 shows the temporal variation of the element concentration and the water level during the sampling period at Lobith. Temporal variation of the element concentrations measured at the other sample locations are presented in Appendix E. The element concentrations were measured from the synoptic suspended sediment samples. In the temporal variation graphs of elements Ca, Zn and Mn, a decrease of the concentrations over time can be observed. For the elements Ca and Zn this decrease is more pronounced than for the measured Mn concentrations, which showed a higher concentration during sample date 16-11-2017. An increase of the measured concentration in the suspended sediment can be observed in the temporal variability graphs for element concentrations of Ti, Rb and Fe. During sample date 16-11-2017, Rb concentrations are remarkably low, which does not fit in the trend. For the elements Cr, Cu, Sr and Pb, no clear reaction could be distinguished from the temporal variability graphs for these elements. The Cr, Cu and Sr concentrations were approximately constant over time. Concentration of Pb decreased in the period between 21-09-2017 and 16-11-2017.

The categorization of elements in terms of the relation between element concentrations and water height in section 4.2.1 was supported by the observed trends in the temporal variability of concentrations in combination with the changing water level over the sampling period. The element concentration of Ca, Zn and Mn in the suspended sediment declined with increasing water level. Secondly, the concentration of the element measured in the suspended sediment increased with increasing water height, which was the case for the elements Ti, Fe and Rb. Thirdly, no distinct reaction on the increasing water level could be identified, which was the case for the elements Cr and Sr.

The main process that caused the declined concentrations of trace metals due to a higher water level was dilution. Mainly the elements Cu, Zn and Pb are characteristic contaminants that are discharged in the river as point-sources, which are prone to dilution and sorption to suspended and bed sediment (Van der Perk, 2006). When a point-source contaminant is mixed with a larger amount of water concentrations of the pollutant will decrease. This is the case when the water level in the river increases or during storm conditions, when clear runoff is transported to the river, resulting in the dilution of the

existing concentrations present in the surface water. Therefore, it can be concluded that elements which are originating from human influences (e.g. industry) show lower concentrations during high water events.

Remobilization of bed sediment into the stream due to erosion and reduced organic matter concentrations in the water are thought to be the main processes causing increased trace metal concentrations measured during high water events. Firstly, as a result of the larger discharge, the wet perimeter increases and hydrodynamics within the channel change. This results in a higher erosion rate of the bed sediment causing an induced sediment load and thus remobilization of sediment originating from sediment storage. Furthermore, the increased wetted perimeter results in the erosion of sinks that are scarcely inundated like floodplains. These sinks contain higher concentrations of trace metals which are brought back in the system during remobilization (Asselman & Middelkoop, 1998). Another explanation for the increased concentrations of some elements with increasing water level is the lowered organic matter concentration in the water. Like the dilution of the concentration of point source pollutants, the organic matter content will dilute during a high water event or simply during increased water levels. There is a strong affinity between metals and organic matter (Forstner & Wittmann, 1981; Lin & Chen, 1997). Organic matter, both in dissolved and particulate form, act as a scavenger for metals in water columns and metal concentrations in sediment show a positive correlation with organic matter content for all metals (Lin & Chen, 1997). As an effect of reduced organic matter concentrations, less trace metal elements will be adsorbed by the organic matter. To summarize, dilution of the organic matter content in combination a decrease of organic matter content resulted in the increased concentrations of trace metals that are present in-situ.

The relation between the concentration variation of the elements and the sediment color on the filter was studied by plotting both the concentration and the color against downstream direction. This made it possible to compare the color changes during different sampling dates. In Figure 13 the relation between the Ti and Zn concentration and sediment color was plotted for sample dates 28-09-2017 and 10-01-2018. For sample date 28-09-2017, only two distinct colors, dull yellow (C=3, V=6) and light yellow (C=3, V=7), were observed. The colors observed during sample date 10-01-2018 are more variable. These colors are: dull yellow (C=4, V=6), yellowish brown (C=3, V=5) and yellow (C=8, V=7). It should be noted that for all studied sediment colors the Hue was 2.5 and during sampling water levels differed considerably, with approximately 600 cm +NAP. Moreover, the concentrations changed between both sample dates. The Ti concentrations increased whereas the Zn concentration decreased. With this change in concentration the colors changed as well. Striking with respect to the sediment color, was the fact that overall the sediment obtained during 28-09-2017 has a dark color whereas the sediment obtained during 10-01-2018 was yellow. The sediment with the yellow color, indicated that the organic matter content in the suspended sediment decreased and the mineral concentration increased with increasing water level. Thus, the sediment color could be used as an indication for concentration variations in suspended sediment although this is an indirect indication. Dark colors indicate high organic matter content in the suspended sediment, indicating an increased element concentration of certain elements as earlier discussed. Furthermore, when sediment colors are light and predominantly yellow, it can be assumed that the mineral content is high and element concentrations like Ti and Rb are higher.

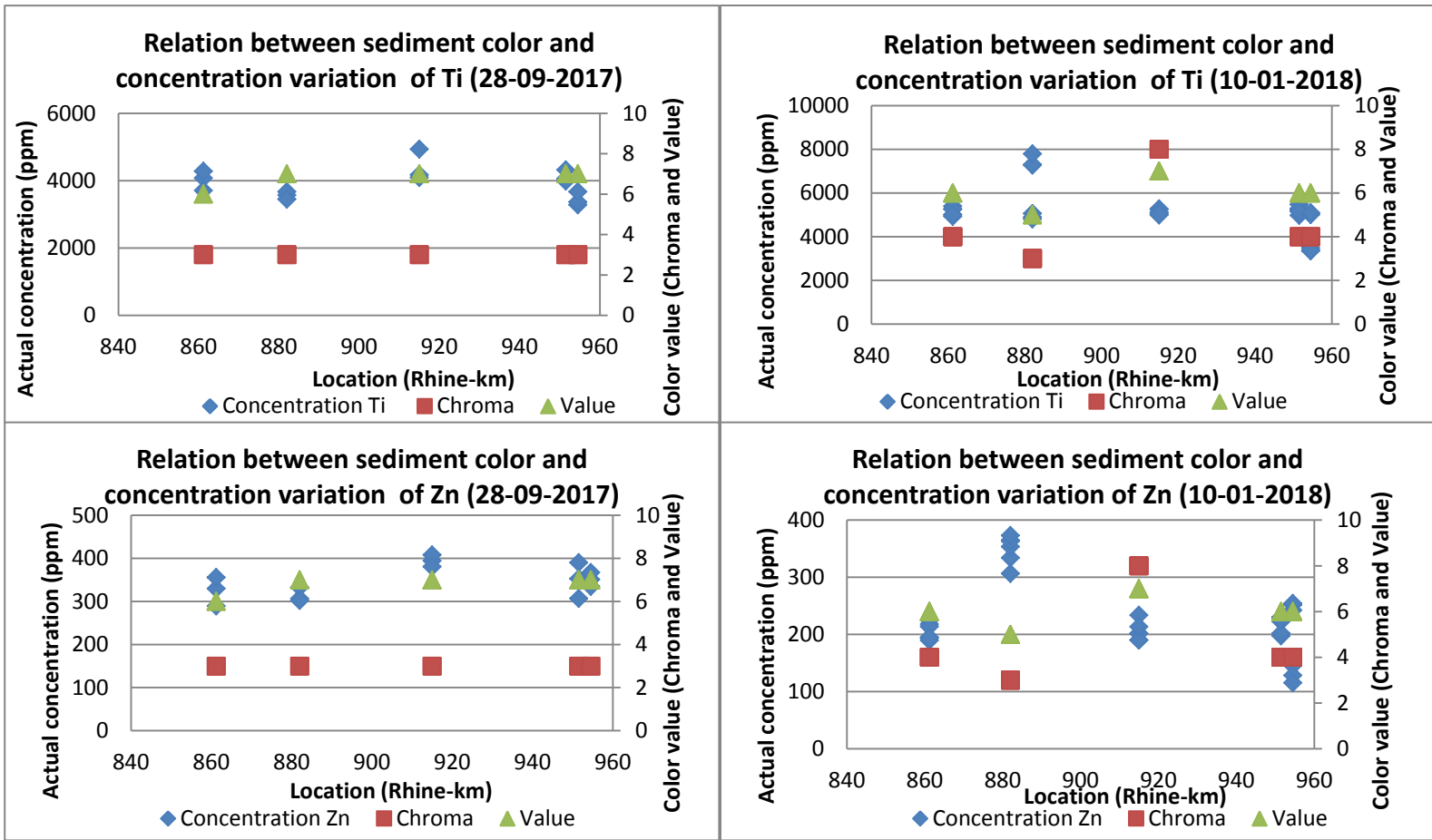
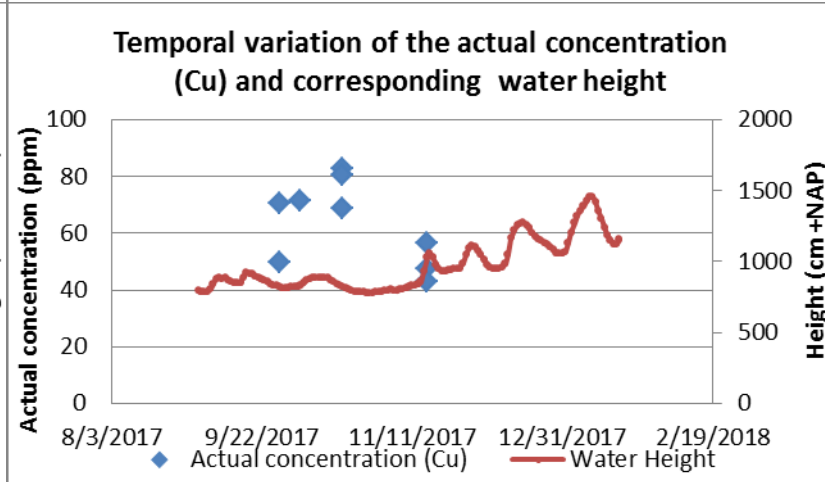
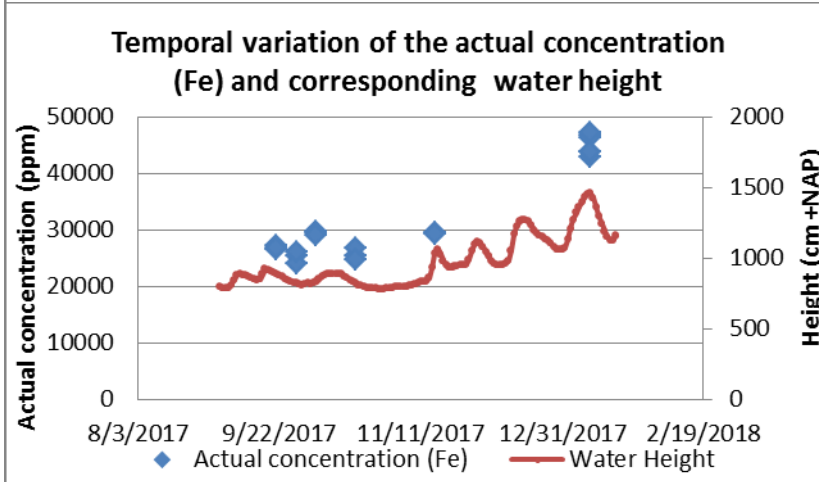
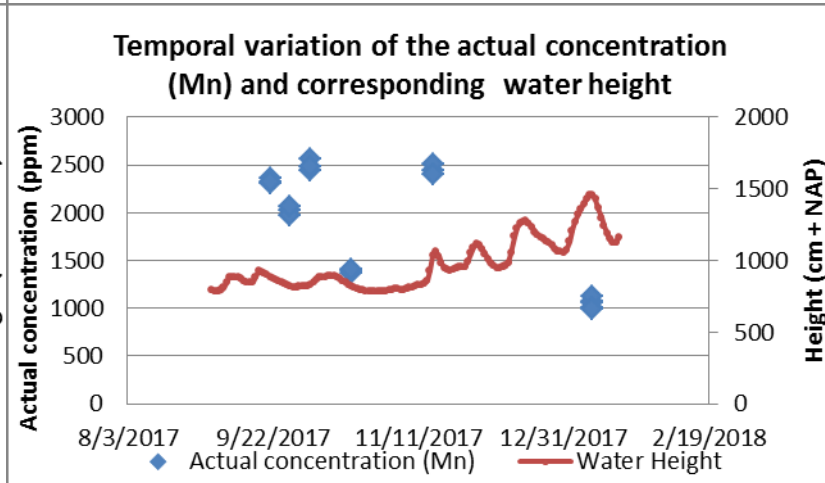
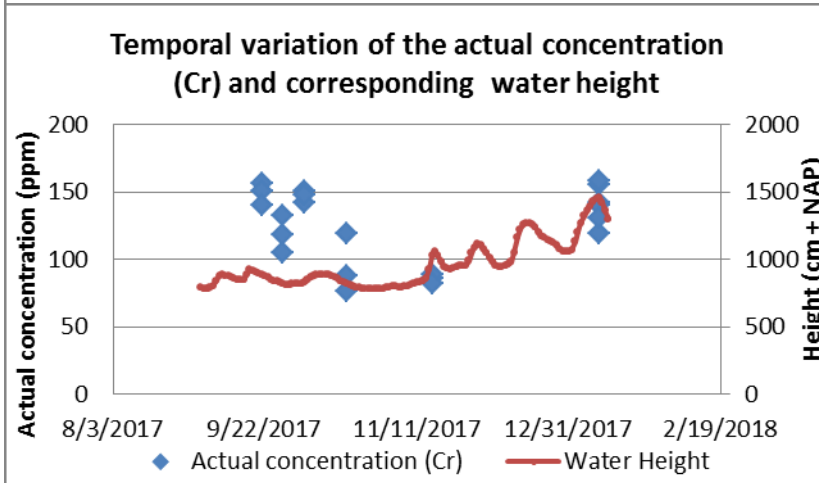
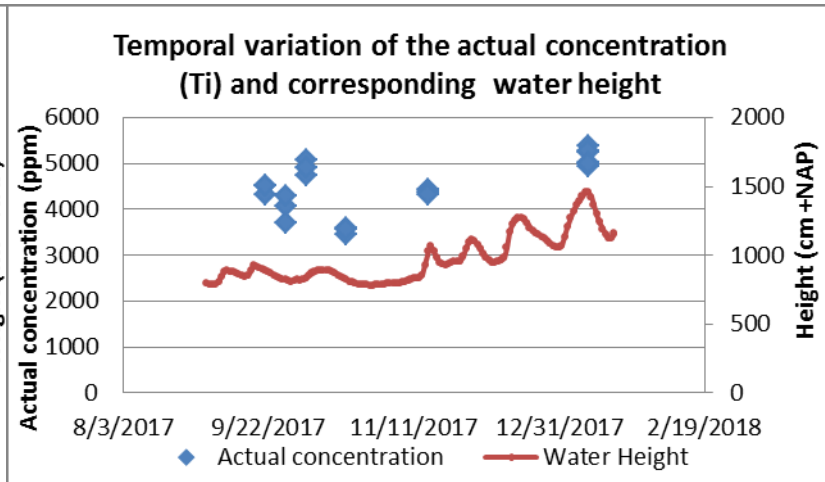
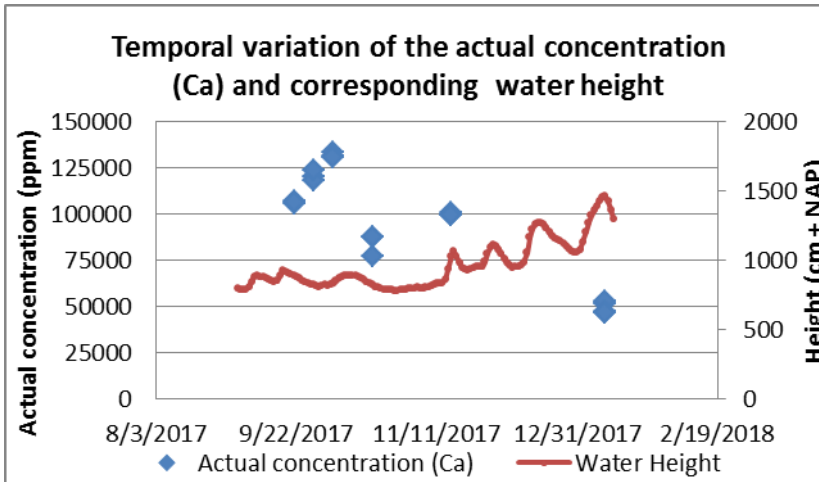


Figure 13: Relation between sediment color and concentrations measured in the suspended sediment.



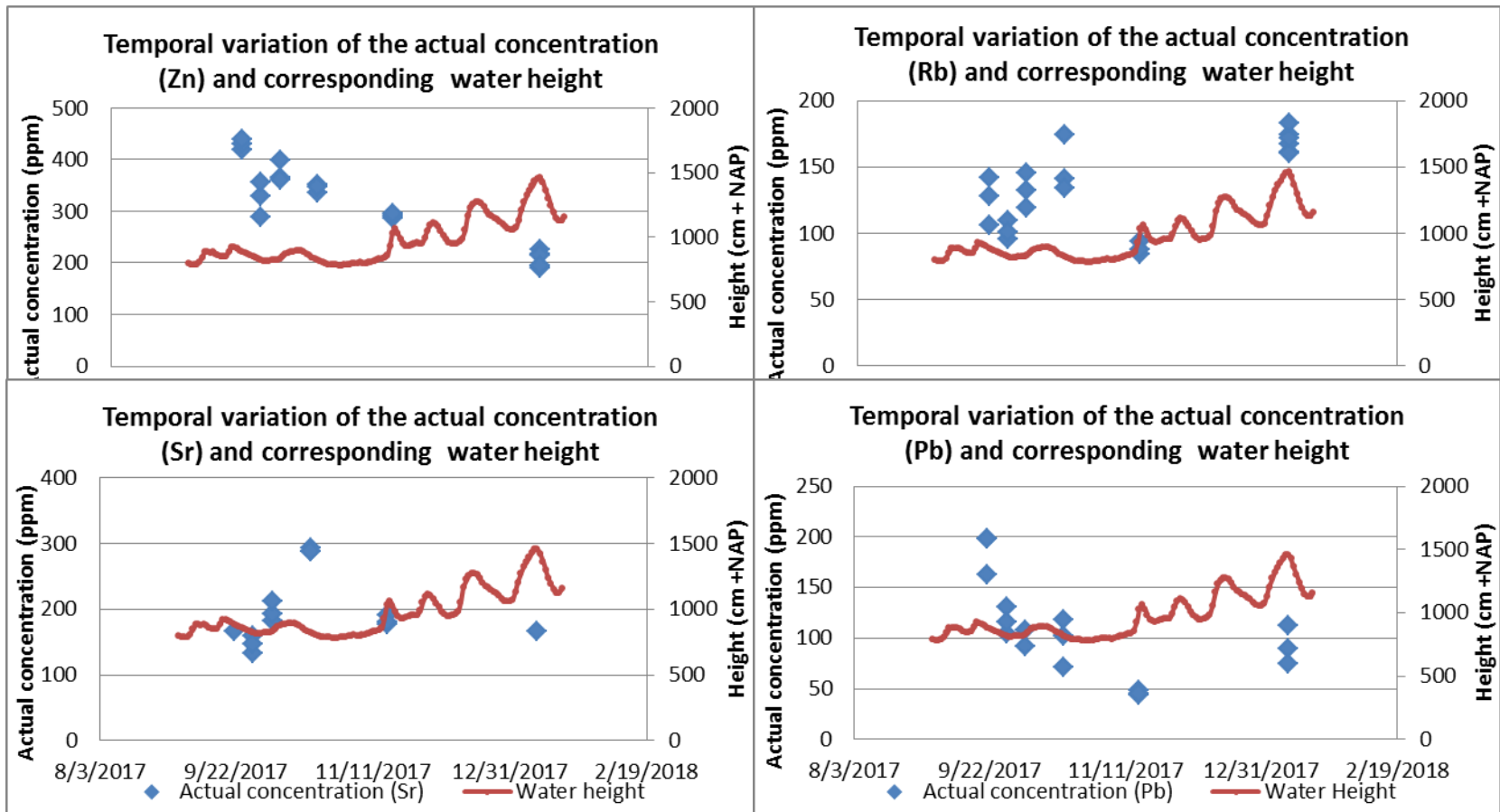


Figure 14: Temporal chemical variation of suspended sediment measured at Lobith in combination with the water level during sampling.

4.2.3 Spatial chemical variation of suspended sediment in the Rhine

The Netherlands

The spatial chemical variability of the trace metals was studied by measuring the concentration of the suspended sediment obtained with water samples and time-integrated Phillips samples from Lobith to Oudendijk. The results for the elements Ti and Zn are displayed in Figure 15 and 16. The variability of Ti and Zn represents the spatial variability of all elements that are divided in the same category as stated in Section 4.2.1. The spatial variability of concentrations measured for all other elements can be found in Appendix F.

Overall, the measured concentrations for Ti do not change much when the sediment flows downstream through the channel from Lobith to Oudendijk (Figure 15). The average concentration measured for Ti throughout the channel was approximately 4500 ppm with a standard deviation of 750 ppm. When the water level in the Rhine increased (during sample date 16-11-2017 and 10-01-2018), the concentration of Ti increased to an average of 5000 ppm. However, even with elevated water levels in the river the concentrations did not vary significantly between the different sample locations. The samples obtained at Lobith and Ooij showed a considerably lower concentration than the other locations. During sample date 16-11-2017, the Ti concentration was approximately 1000 ppm lower than the concentrations measured at Wamel, Vuren and Oudendijk. Measured concentrations were constant during high water conditions on 10-01-2017. The concentration measured with the time integrated Phillips sampler showed a constant concentration as well.

A similar behavior can be observed for the measured Zn concentrations from Lobith to Oudendijk. The average measured concentration was approximately 350 ppm with a standard deviation of 100 ppm during normal conditions. However, the sample dates during high water showed considerably more spatial variation in the concentration throughout the channel from Lobith to Oudendijk. The trend that can be seen in the changing Ti concentration during 16-11-2017, was prominent in the changing Zn concentrations as well. Even though these elements belong to different reaction groups according to Section 4.2.1, for both elements the concentration is significantly lower at Lobith and Ooij than the concentrations measured at Wamel, Vuren and Oudendijk. During high water condition on 10-01-2018, the average Zn concentration is decreased but the concentration throughout the channel is constant if the concentrations measured at Ooij are excluded. The time-integrated Phillips sampler shows a constant Zn concentration throughout the channel as well. However, the average concentration throughout the channel was somewhat higher in comparison to the concentrations measured from the water samples.

To conclude, the concentration of both elements, that are representing the element groups stated in table 3, stay relatively constant throughout the channel with exception of the spatial distribution during 16-11-2017. The first collected samples of this day showed lower concentrations than the later obtained samples at Wamel, Ooij and Oudendijk. During this day, the flood peak propagated through the channel. Maximum discharge was not reached yet when the samples were taken at Lobith and Ooij. However, when the samples were obtained at Wamel, Vuren and Oudendijk the maximum discharge was already passed. The fact that the elements show the same reaction is striking, since Ti and Zn are categorized in

different groups in Table 3. During the first two sample moments the peak was not reached resulting in average concentrations of Ti but the slightly lower Zn concentration. Since the remobilization rate of the bed sediment is low, the main factor that can cause the declined Zn concentration is dilution. When the peak passed through the channel, the samples were taken at Wamel, Vuren and Oudendijk which were located behind the flood wave at this time. At this moment in time the main factor is remobilization of the bed sediment causing increased concentrations for both elements. Because the short period in which the elevated water level occurred, sediment could sink to the river bed again, resulting in a fast decrease of Zn concentrations in the water since Zn is mainly attached to the sediment and will not dissolve.

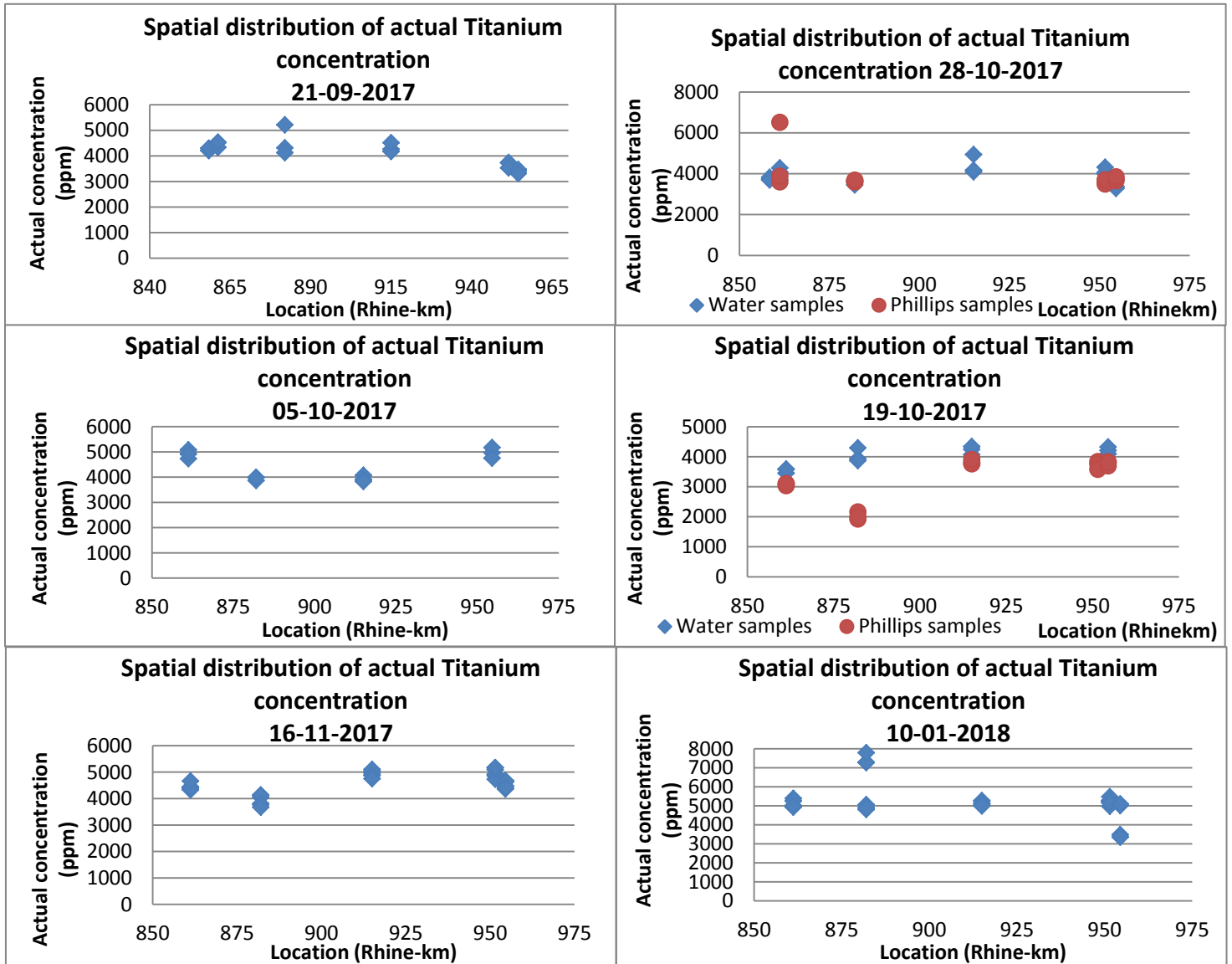


Figure 15: Spatial and temporal distribution of the Titanium concentration from Lobith to Oudendijk (The Netherlands).

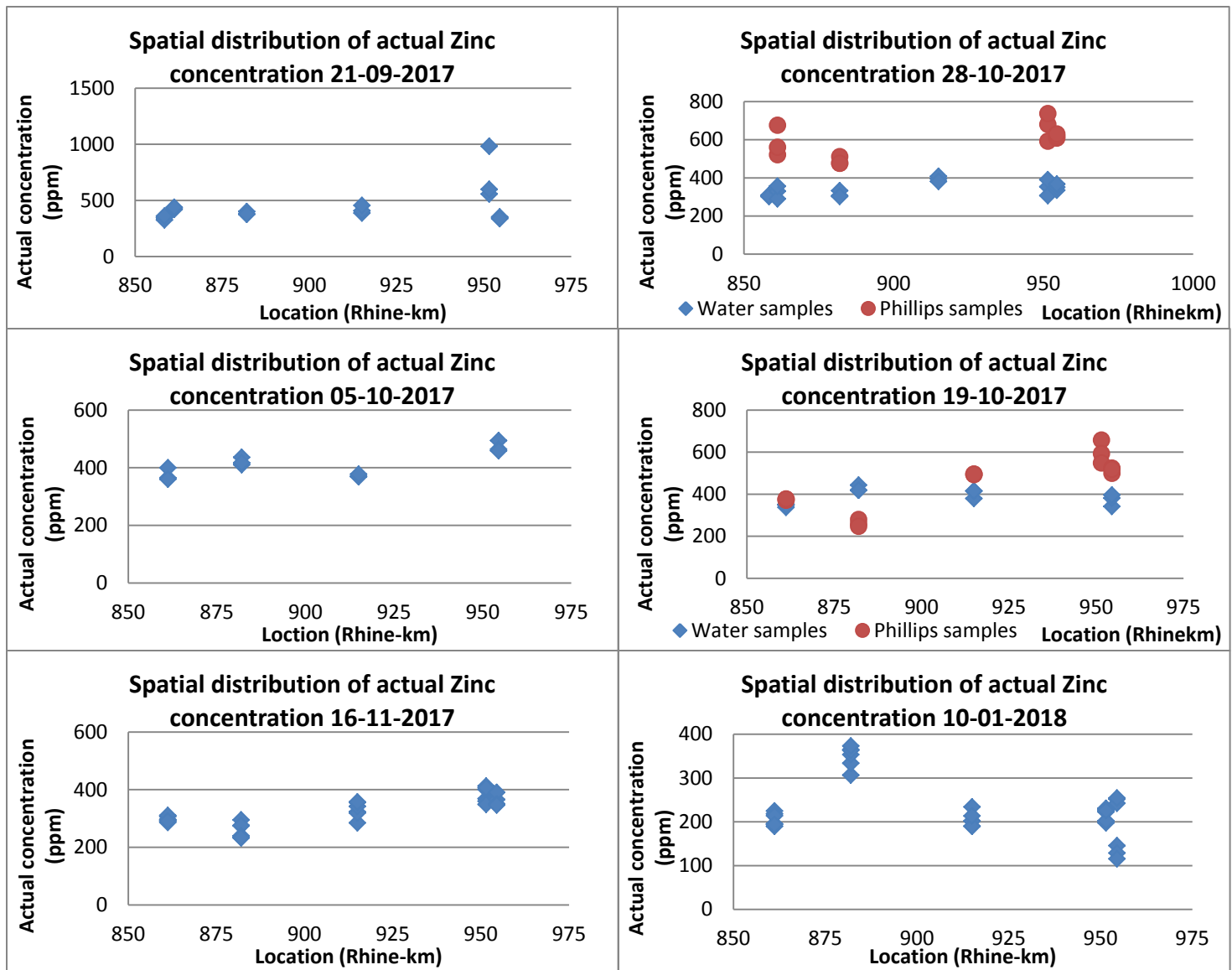


Figure 16: Spatial and temporal distribution of the Zinc concentration from Lobith to Oudendijk (The Netherlands).

Germany

During fieldwork, suspended sediment and bed sediment samples were obtained for approximately every 40 km of the Rhine. Moreover, suspended sediment and bed sediment samples were collected from the major tributaries Neckar, Main, Lahn and Ruhr. From the Mosel, only suspended sediment samples were collected since the Mosel was completely embanked along the sample location which made it impossible to take bed sediment samples. The concentrations measured for each element obtained from suspended and bed sediment samples are shown in Figure 17.

The concentrations of the elements that were measured in the suspended sediment showed for most elements increased concentrations in downstream direction. There were no major fluctuations and the concentration stayed fairly constant from Basel to Rheinberg. Trace metals Sr, Cr, Rb and Pb showed a

slight decrease of concentration in downstream direction. For all three elements, the decreased concentrations coincided with the inflow of the tributary Neckar. All other trace metals (Ti, Mn, Fe and Zn), showed a slight increase in concentrations in downstream direction. When comparing the measured concentrations in the tributaries with the concentrations measured in the main branch, the tributaries Lahn and Ruhr stand out. The suspended sediment that was transported through both tributaries showed a significantly higher concentration of all elements, except for Ti. However, at the sample locations just downstream of the confluence of the tributaries with the main branch, the concentrations were not higher compared to the concentrations measured before the confluence. The suspended sediment that was transported through the tributary Mosel showed only higher concentrations for the elements Cr, Mn, Rb and Pb, which was similar to the concentrations measured in the Lahn. The chemical concentrations of the suspended sediment in the Neckar and Main are comparable with the concentrations measured in the main branch of the Rhine.

For all measured elements the concentration measured in the bed sediment increased from Basel to Rheinberg, with highest concentrations reached between 600 and 780 Rhine-km. An exception is the concentration measured for Sr, which showed a steady to slightly decreasing concentration in the bed sediment. The bed sediment obtained from the tributaries Main and Lahn stood out when the concentrations were compared with the concentrations measured in the bed sediment of the main branch of the river Rhine. The Main showed high concentrations for the elements Mn and Fe and a low concentration for the element Rb. The measured concentrations of the elements Zn and Ti in the tributary Lahn were high compared with sediment from the main branch whereas the concentration measured for Sr is rather low. All trace elements measured in the tributary Ruhr showed elevated concentrations, except for Sr that showed a significantly lower concentration, compared to the main branch of the Rhine.

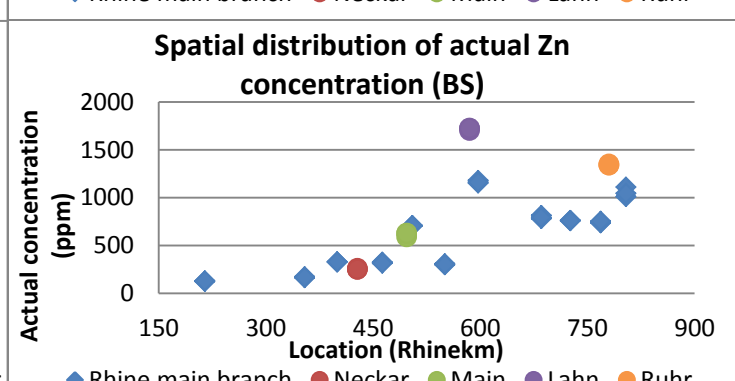
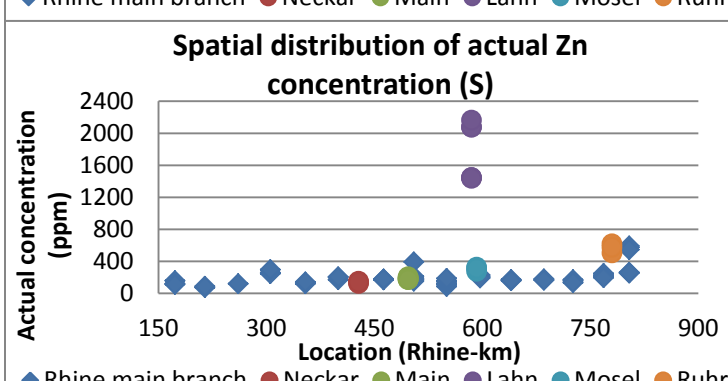
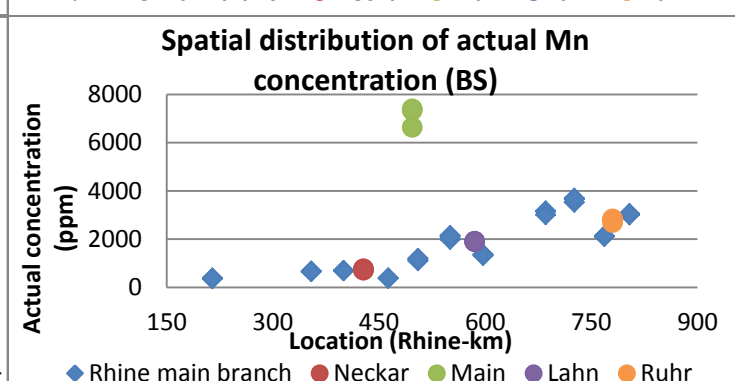
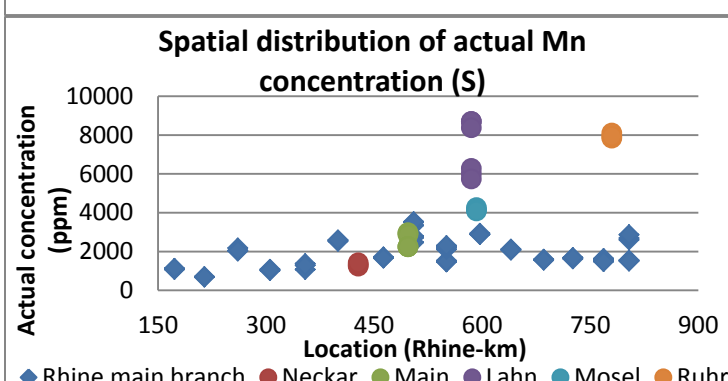
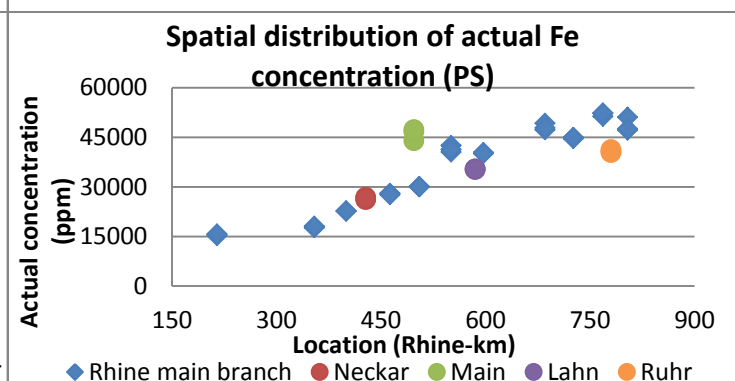
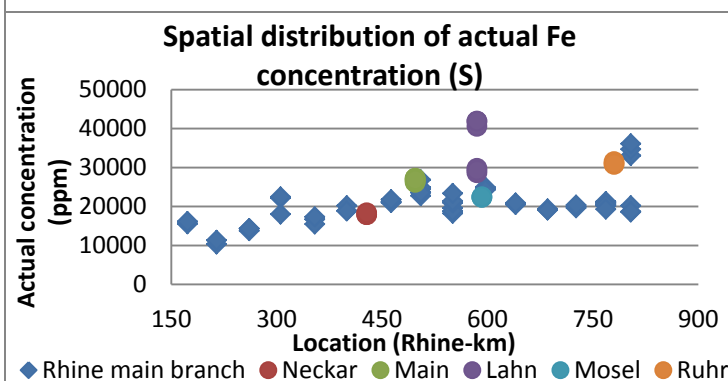
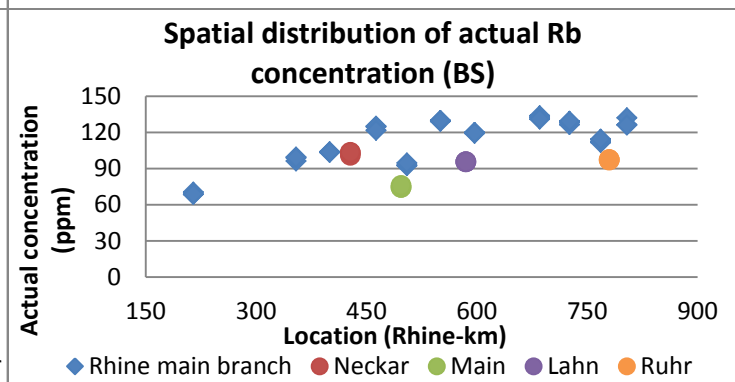
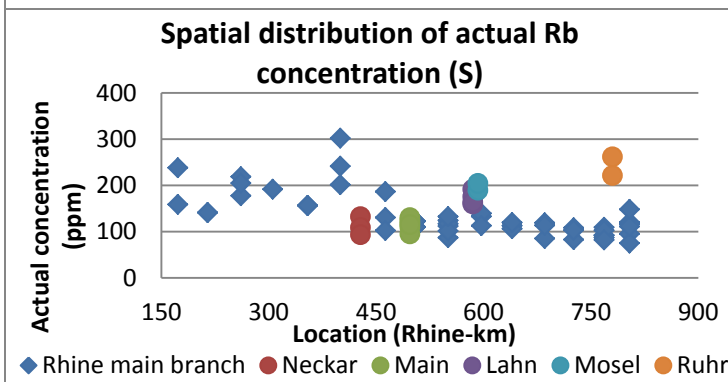
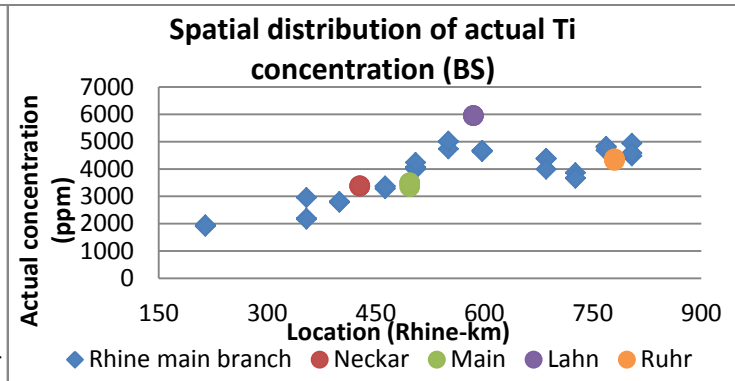
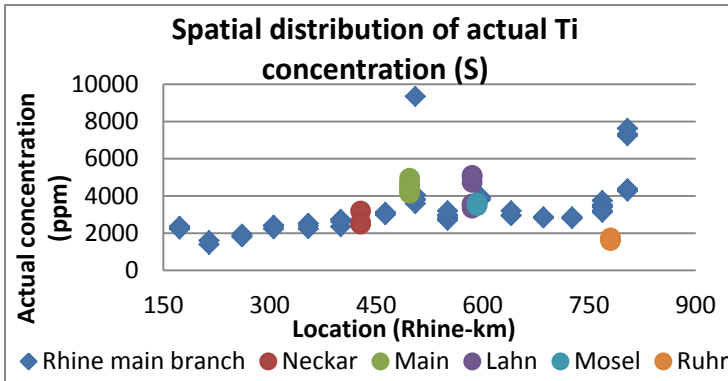
The concentrations measured in the bed sediment are not comparable with the concentrations measured in the suspended sediment throughout the reach of the Rhine. The measured concentrations in the bed sediment are substantially higher than the concentrations found in the suspended sediment at the same location. The rate at which the concentration increased in downstream direction is higher for the bed sediment along the Rhine as well. The degree at which the concentrations change in downstream direction for both kind of sediment is dependent on the element. Again, the elements that were categorized in Section 4.2.1 can be applied on these graphs. The high concentrations measured in the suspended and bed sediment after the Ruhr River confluences with the main branch of the Rhine is most striking. The concentrations measured in the bed sediment were higher than the measured concentrations in the suspended sediment. This also applied to the other tributaries, for which the concentrations in the bed sediment were in every case higher than in the suspended sediment.

The chemical composition of the suspended sediment suggests that the trace elements originated mostly from the upstream area of the catchment and that the composition did not change significantly when the sediment was transported through the channel. The slight increase or decrease of the concentration of trace metals indicated that there was some interaction between the suspended load through the channel and the bed sediment. In addition, the variation of the concentrations of trace metals can be caused by the confluence of tributaries. However, processes that influenced variation between sample

locations the most were mostly anthropogenic, like point-source pollution from a factory. The increasing concentrations of the trace metals within the bed sediment revealed that the bed is mostly behaving like a sink, in which the pollution of the industry upstream was taken up by the sediment. As can be expected for a pollutant to be taken up by sinks along a river, the concentrations of the trace metals within the bed sediment increased in the downstream direction. The interaction between suspended sediment and the bed sediment for trace metals Ti, Cr, Mn, Fe and Zn is small. As a result, the concentration for these metals increased slightly in downstream direction due to a low level of release from the bed sediment. However, the interaction between the suspended sediment and bed sediment was more profound in the concentration variation of Rb, Sr and Pb. These metals showed a slight decrease in concentration in the downstream direction measured in the suspended sediment. Moreover, the concentrations of these trace metals showed an increased concentration in the bed sediment. Since these measured concentrations represented a snapshot in time, no clear clarification could be given with regard to the selectivity of presumed metal uptake by bed sediment.

The concentrations of trace elements measured in the sediment of the tributaries of the Rhine showed a strong variation of concentrations between the tributaries. Moreover, peaks of trace metal concentrations varied between the major tributaries of the Rhine. From Figure 17 can be concluded that the tributaries Lahn, Mosel and Ruhr were the most polluted tributaries. According to Martin (2000; 2004) the Lahn River is highly polluted as a result of the intensive industrial waste water discharge into the river. Metal concentrations of Cd, Cu, Zn and Pb were markedly higher measured in the study of Martin (2000; 2004), than background concentrations. This was confirmed by the measured concentrations in this study, in which the concentrations of Zn and Pb measured in the river Lahn were substantially higher than in the main branch of the Rhine. Overall, the elevated concentrations of trace metals did not exceed the concentrations that are measured in the bed sediment. However, in the Lahn River pollution of the river water was still ongoing. Therefore, the concentrations of the trace metals in the suspended sediment exceeded the concentrations in the bed sediment. A similar effect was mentioned by Imhoff et al. (1981), which studied the pollution in the Ruhr. From this study there could be concluded that the trace metal concentrations of Pb, Cu, Zn, Ni, Cr and Cd were considerably high. According to Klaus et al (1981), concentrations of the trace metals Pb, Zn and Cr are significantly high in the sediment of the Ruhr. The high concentrations of Pb, Zn and Cr measured in the sediment during this study confirmed the rate of pollution that was stated in the study of Klaus et al. (1981). To summarize, the tributaries Lahn, Ruhr and Mosel were highly polluted by anthropogenic influences, which caused higher concentrations in both the suspended and bed sediment.

The elevated concentrations of trace metals measured in the suspended sediment in the tributaries, do not cause increased concentrations in the main branch after the tributary confluences with the Rhine. Figure 3 shows the average discharge of the tributaries and that of the main branch of the Rhine. The discharges of the tributaries are very small compared to the discharge flowing through the Rhine. As a result, the trace metal concentration in suspended sediment that was transported through a tributary was diluted when it flowed into the Rhine. This means that even though the concentrations of the tributaries are relatively high compared to the Rhine, the high trace metal concentration fade away



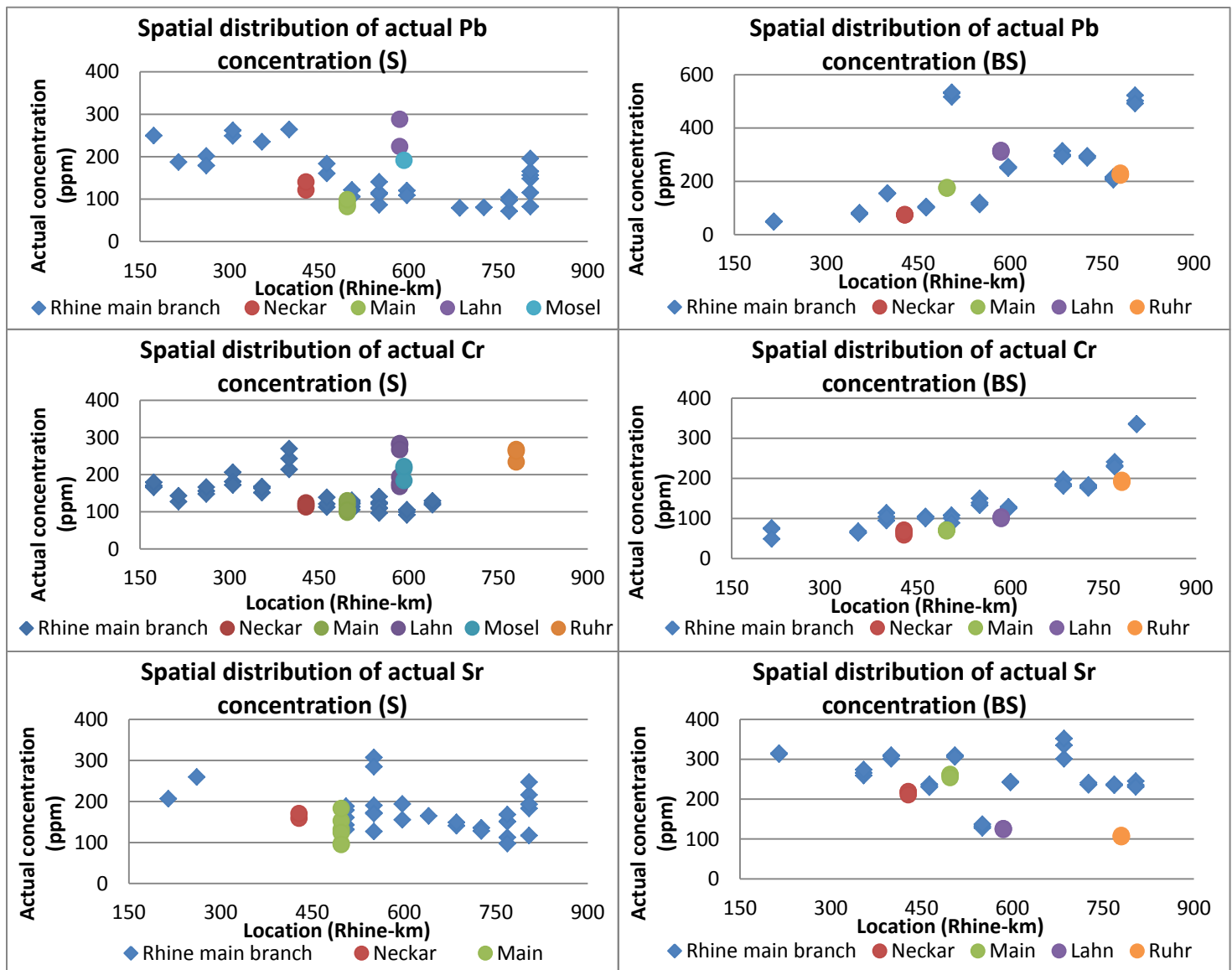


Figure 17: Spatial chemical variation of suspended sediment and bed sediment measured by obtained suspended sediment (S) and bed sediment samples (BS)

when the tributary merges with the main branch. The elevated concentrations that occurred after the confluence of the river Ruhr into the Rhine were still present in the measured concentrations of the Dutch part of the Rhine. Measured concentrations of the trace metals in suspended sediment from Lobith to Oudendijk (The Netherlands) showed for example an average concentration of 4000 and 400 ppm for Ti and Zn respectively (Figure 15 and 16). This was a comparable concentration that was measured after the confluence with the Ruhr River.

5 Conclusions

The use of direct XRF measurement of element concentrations of suspended sediment extracted from the filtration of water samples using membrane filters requires a substantially lower volume of water, to reach the sediment weight threshold on the filter, compared to established measuring techniques. The XRF analysis provides usable measurements for the elements Ca, Cr, Fe, Zn, Mn, Pb, Rb, Ti and Sr obtained from synoptic suspended sediment samples. Elements that were measured by the XRF in the time-integrated samples but that were not measured in the synoptic samples are As, Ba, Sn and Hg. Signals for As, Ba, Cd, Cu, Co, Mo, Ni, Sb, Sn and Zr were often or always below the detection limit. The precision of the element concentrations measured in the synoptic suspended sediment samples was related to the sediment weight present on the filter. As criteria for estimating a proper element concentration from the water samples, a threshold (>0.01 g) was defined for the sediment weight. In order to compare measured concentrations obtained from the water samples with the concentrations from the sediment samples obtained by the Phillips sampler, the concentrations of the water samples were corrected. This was done by estimating a correction parameter with random filtration of a resuspended sediment sample with known concentrations. The calculated actual concentrations resembled the measured concentrations of the sediment collected with the Phillips sampler. Furthermore, the measured element concentrations of the suspended sediment obtained using both techniques were highly comparable to the long-term average concentrations of measured by Rijkswaterstaat.

The temporal variability of the measured element concentrations obtained from the synoptic suspended sediment samples provided a subdivision into three categories of the measured elements. The elements Ti, Fe and Rb showed a positive correlation with changing water levels, meaning that the concentrations of these elements increased with increasing water level. The elements Ca, Mn, and Zn showed a negative correlation with increasing water levels, meaning that the concentrations of these elements decreased with increasing water levels. Elements Sr, Cr, Cu and Pb did not show large variations. These relations were supported when the measured concentrations were compared with varying water levels and sediment colors. The main process that caused the declined concentrations of trace metals due to a higher water level was dilution. Mainly the elements Cu, Zn and Pb are characteristic contaminants that are discharged in the river as point-sources, which are prone to dilution. This is the case when the water level in the river increases or during storm conditions when, clear runoff is transported to the river, resulting in the dilution of the existing concentrations present in the surface water. Remobilization of bed sediment into the stream due to erosion and reduced organic matter concentrations in the water was an important process causing increased trace metal concentrations during high water events. Another process that resulted in increased concentrations of trace metal concentrations with increasing water level was the lowered organic matter concentration in the water. Organic matter, both in dissolved and particulate form, act as a scavenger for metals in water. As an effect of reduced organic matter concentrations, less trace metal elements will be adsorbed by the organic matter.

The spatial variation of element concentration obtained from suspended sediment samples of the German part of the Rhine showed no major fluctuations and the concentration stayed fairly constant from Basel to Rheinberg. Trace metals Sr, Cr, Rb and Pb showed a slight decrease of concentration in

downstream direction. All other trace metals (Ti, Mn, Fe and Zn) showed a slight increase in concentrations in downstream direction. The bed sediment showed increasing concentrations in downstream direction except for Sr which decreased slightly. The increasing concentrations of the trace metals within the bed sediment indicated that sediment is mainly stored in the channel bed sediment, in which the pollution of the industry upstream was taken up by the sediment. The interaction between suspended sediment and the bed sediment for trace metals Ti, Cr, Mn, Fe and Zn is small. As a result, the concentration for these metals increase slightly in downstream direction due to a small rate of release from the bed sediment. However, the interaction between the suspended sediment and bed sediment was more profound in the concentration variation of Rb, Sr and Pb which showed a slight decrease in downstream direction. The tributaries Lahn and Ruhr show significant higher concentrations for both the suspended and bed sediment, confirming major pollution in this part of the catchment.

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Appendix A: X-Ray Fluorescence (XRF) analysis

XRF spectrometry determines the elemental composition of a material. This method identifies elements in a substance and quantifies the amount of those elements present. An element is defined by its characteristic X-ray emission wavelength or energy. The amount of an element present in a sample is determined by measuring the intensity of the characteristic spectral line for each element.

The handheld XRF device is an analytical technique that allows both quantitative and qualitative analysis of the composition of a sample in a non-destructive way, without the need for site specific standards (Kalnicky & Singhvi, 2001). The X-ray fluorescence spectrometer has been used in the laboratory for years. However, the handheld XRF technology is a relative new device, which gained a widespread acceptance in the environmental community as a viable analytical approach. This is due to the combination of highly sensitive detectors and associated electronics with efficient radioisotope source extraction.

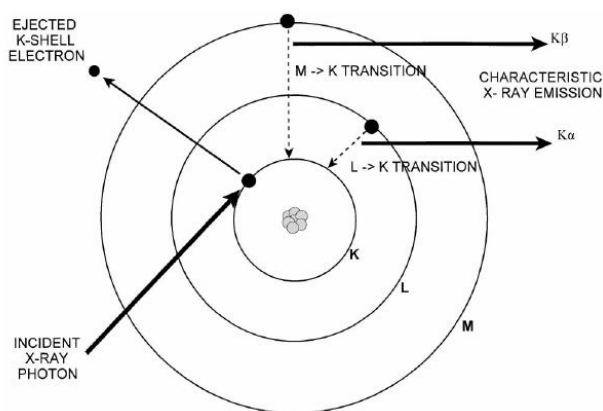


Figure A1: Electron orbitals and the mechanism for X-ray Fluorescence of an atom (Kalnicky & Singhvi, 2001).

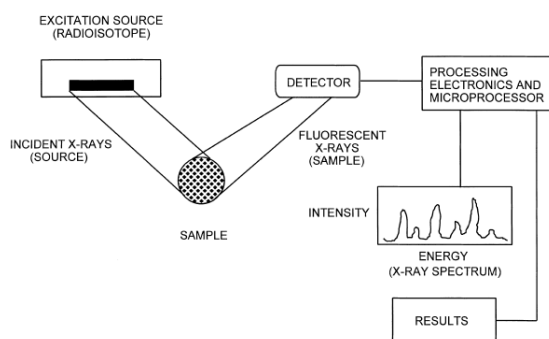


Figure A2: Main components of a handheld XRF and the chain of process in order to get a result (Kalnicky & Singhvi, 2001).

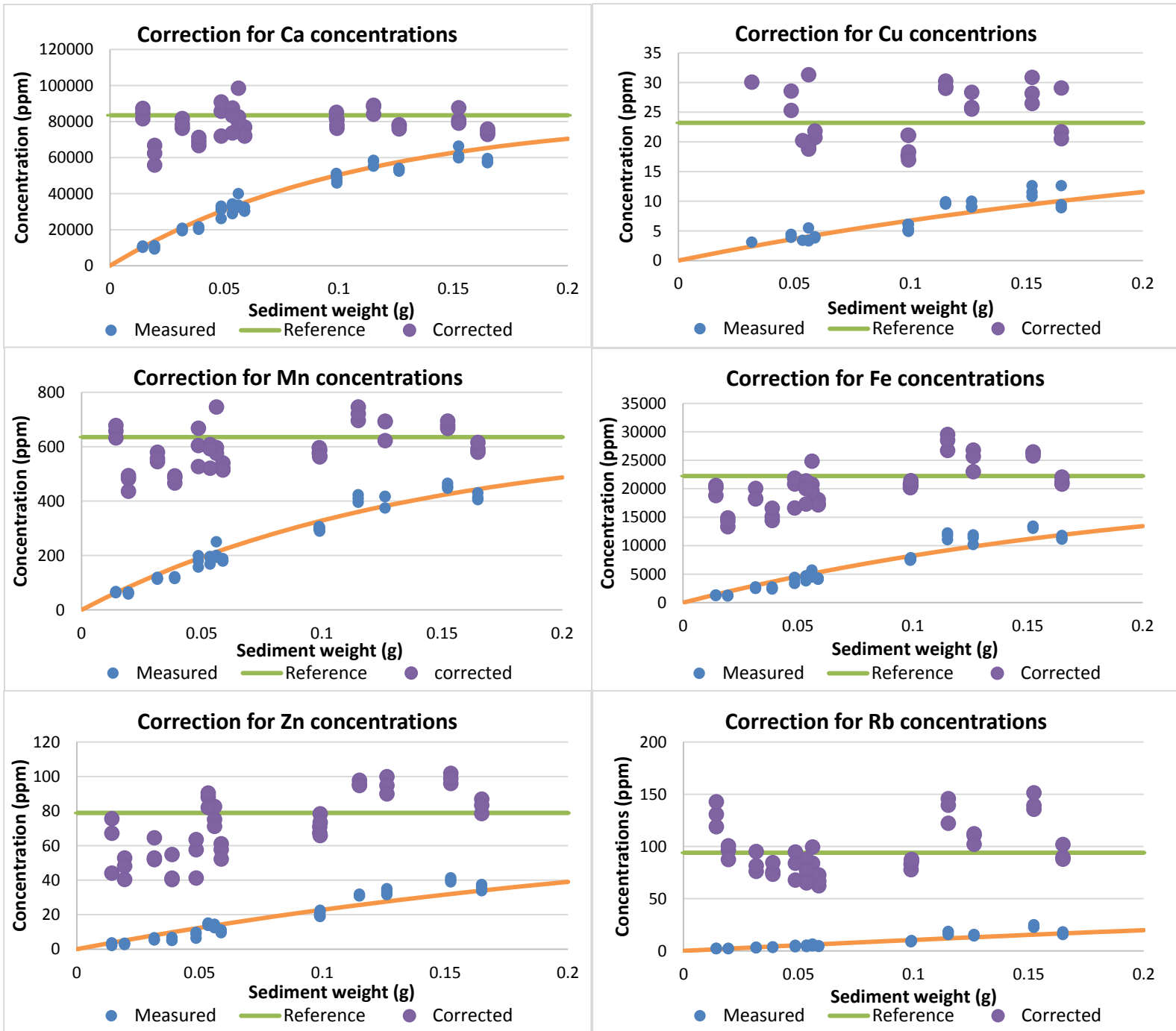
All atoms have a fixed number of electrons arranged in orbitals or shells around the nucleus. XRF spectrometry typically uses activity in the first three electron orbitals, the so called K, L and M lines, where K is closest to the nucleus of the atom (Figure A1). Each electron orbital corresponds to a specific and different energy level for a given element (Olympus, 2013). The handheld device activates samples with X-rays so that the reflected energy is detected and analysis of elements in the sample is possible. This process will be further explained and is graphically showed in Figure A1 and A2.

High-energy primary X-ray photons emitting from a source, in this case an X-ray tube, strike a sample during XRF analysis. Since primary photons from the X-ray source have enough energy, an electron is thrown out of the inner K or L orbit causing a vacancy in the inner atom shell. Because electrons tend towards stability and the atom becomes an unstable ion, an electron from an outer orbit (L or M) moves into the vacancy in the inner shell (Figure A1). The movement from the outer orbit into the inner orbit causes emission of energy known as a secondary X-ray photon. This energy is equivalent to energy in the X-ray region of the electromagnetic spectrum also called fluorescence. Because every atom has an X-ray line spectrum, the X-rays emitted are characteristic of the atom and thus provide qualitative identification of the element. The difference in energy between the initial and final electronic state of

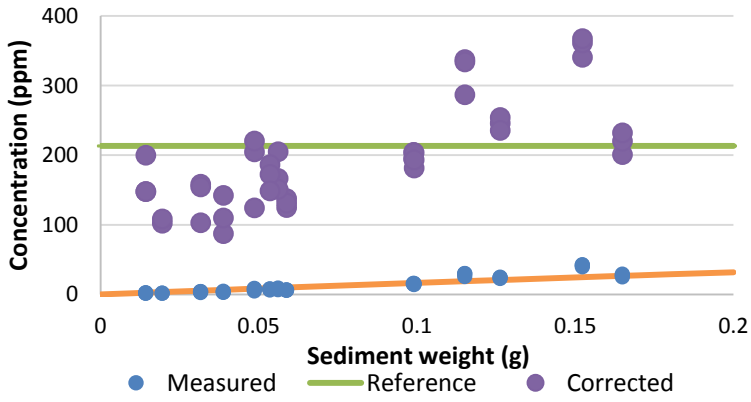
the transition is equal to the photon energy of a spectral line. By activating the sample a spectrum of X-rays is created by all the elements present in the sample. Since a distinct X-ray will be emitted for each type of transition, each present element will have many characteristic lines in the spectrum. The number of element specific characteristic X-rays produced in a sample over a given period is measured and determines the quantity of an element present in the sample (Olympus, 2013).

In Figure A2 the main components of the XRF analysis are shown. The activating source is used to irradiate the sample which in turn fluoresces. XRF devices with only one radioisotope source are not sufficient for activating the entire range of elements of interest in the analysis. Therefore, many devices use two or more sources to maximize element range. However, radioisotopes have a half-life time, meaning that the source could lose its amount of energy to activate the samples. The handheld XRF used for this study therefore is equipped with an X-ray tube to activate the samples after which the characteristic spectrum of X-ray lines is detected and then processed by a computer. The used XRF emitted X-rays in three beams with decreasing intensity. The beams consist of 50kV, 40kV and 15kV respectively and had a radiation time of 60 seconds to activate the sample.

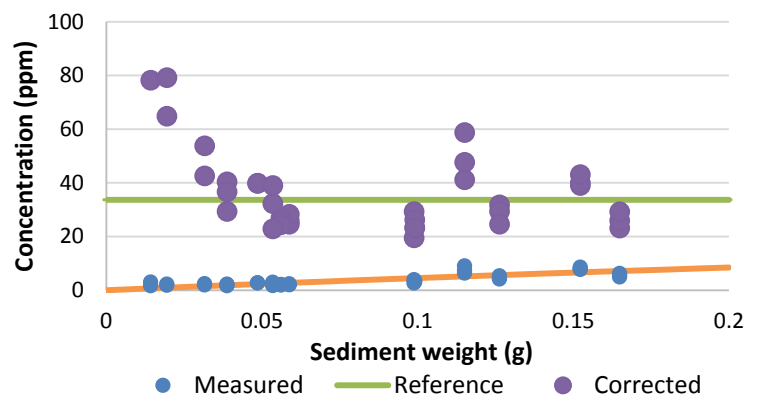
Appendix B: Validation of corrected concentrations with reference concentration



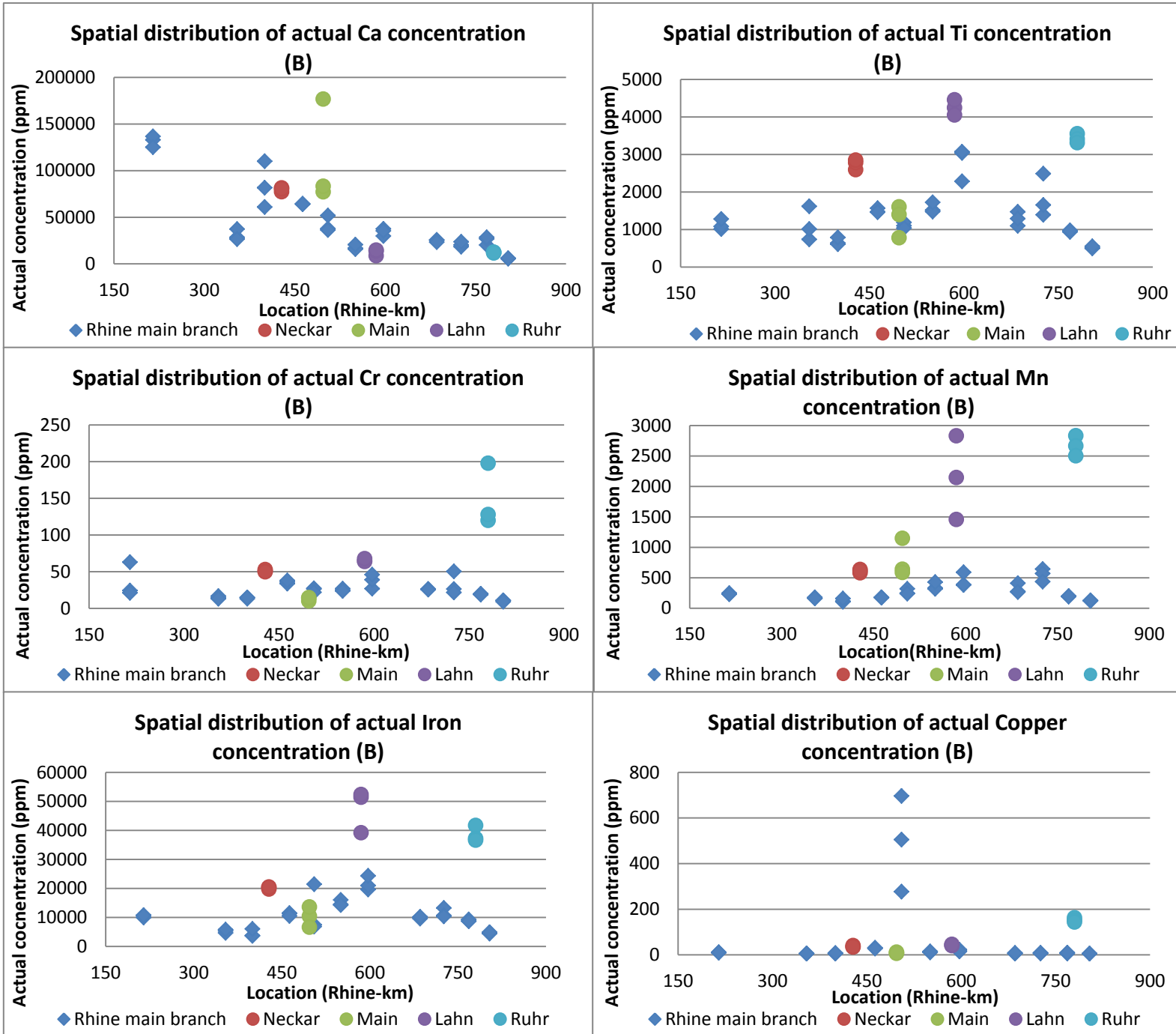
Correction for Sr concentrations

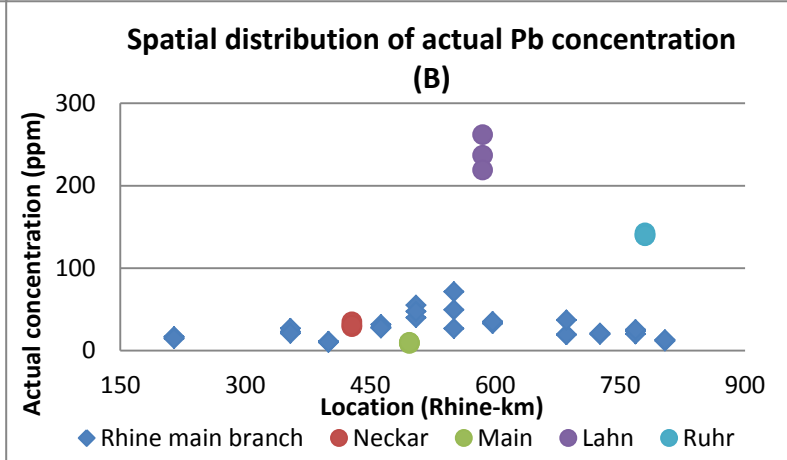
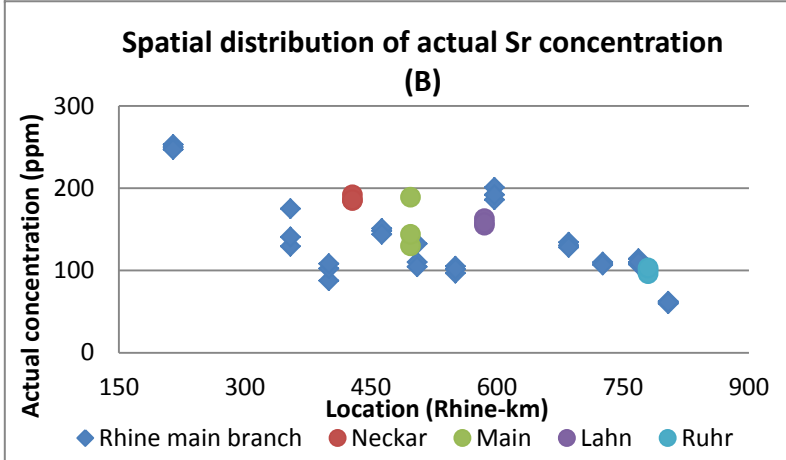
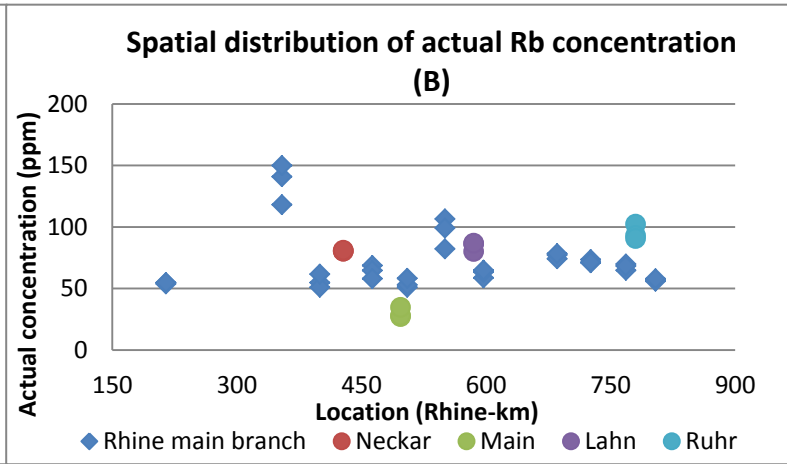
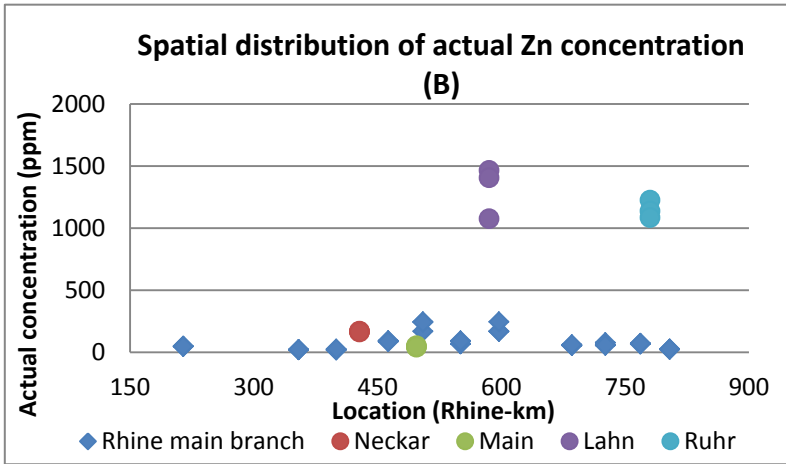


Correction for Pb concentrations



Appendix C: Concentrations measured in bulk bed sediment





Appendix D: Correlation coefficients

Correlation Ooij

	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Rb	Sr	h
Ca	1									-0.81351
Ti	-0.42239	1								0.748068
Cr	-0.13527	0.841776	1							0.471121
Mn	0.133463	-0.14537	-0.20076	1						-0.45736
Fe	-0.52629	0.955687	0.772943	-0.27114	1					0.866852
Cu	0.794489	0.513889	0.893057	-0.31227	0.204794	1				-0.88679
Zn	0.644243	0.245728	0.436745	-0.18581	0.131781	0.935202	1			-0.19975
Rb	0.555089	0.19224	0.647311	-0.26443	-0.07388	0.88293	0.565721	1		-0.69222
Sr	0.790665	0.185139	0.079201	-0.2804	0.451078	0.59428	0.763934	0.163312	1	-0.53917
Pb	0.464246	0.354841	0.624345	-0.35123	0.330712	0.878438	0.757684	0.534975	0.70881	0.009389

Correlation Wamel

	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Rb	Sr	h
Ca	1									-0.95584
Ti	-0.73146	1								0.791272
Cr	-0.7484	0.644272	1							0.776289
Mn	0.607153	-0.15881	-0.71833	1						-0.63331
Fe	-0.95046	0.782326	0.830263	-0.67097	1					0.994129
Cu	0.136039	-0.04353	0.595966	-0.35984	-0.37536	1				-0.48525
Zn	0.895108	-0.75445	-0.6847	0.600749	-0.9303	0.371329	1			-0.95176
Rb	-0.86053	0.713151	0.888003	-0.72745	0.905475	0.768568	-0.80065	1		0.874113
Sr	0.537297	0.09954	-0.19638	0.055643	-0.0318	-0.29519	-0.26755	-0.33392	1	0.029817
Pb	-0.04005	-0.37797	0.321951	-0.70123	-0.05188	0.683873	0.048618	0.349575	-	-0.15521
									0.27287	

Correlation Vuren

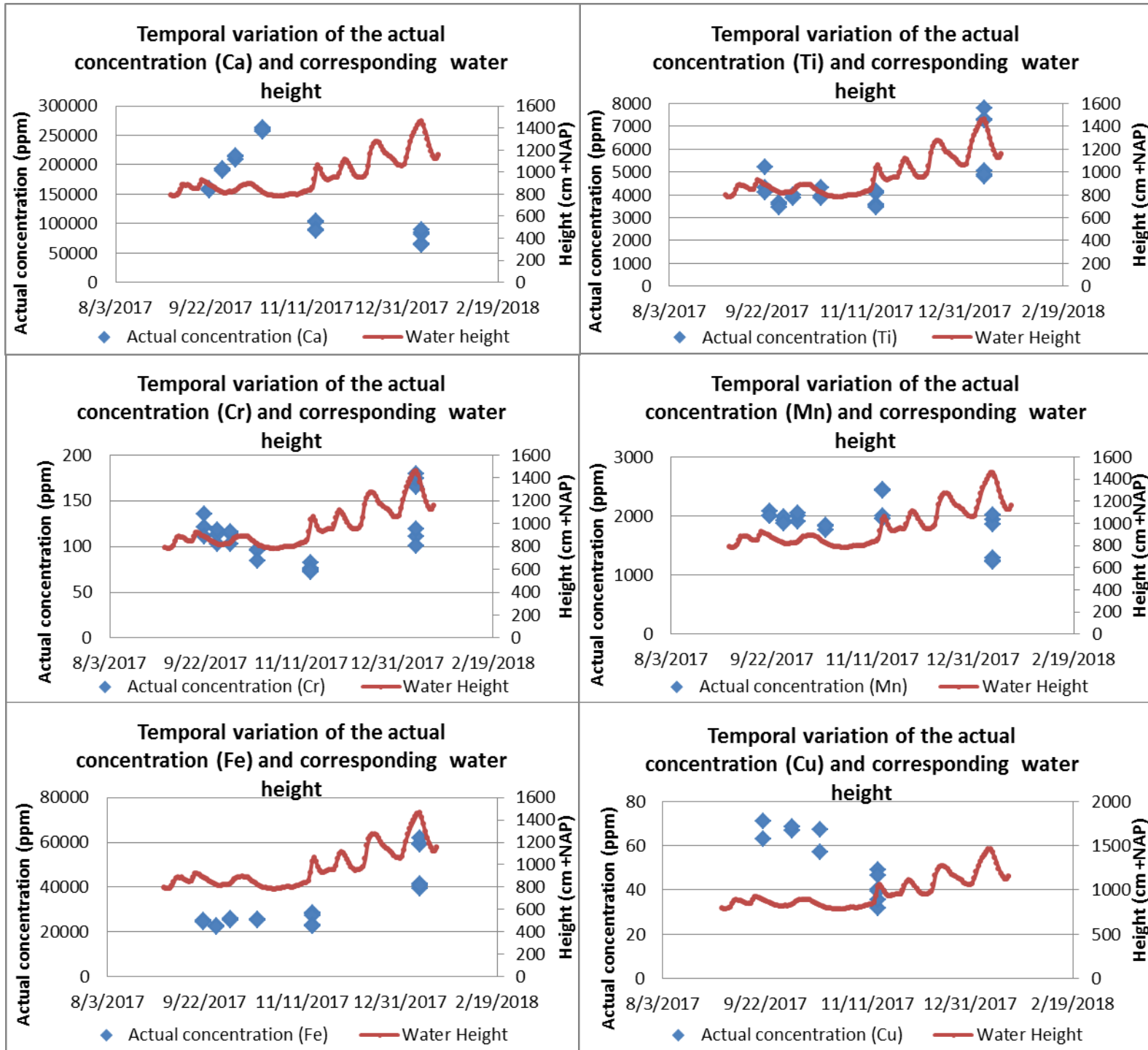
	Ca	Ti	Cr	Mn	Fe	Zn	Rb	Sr	h
Ca	1								-0.85545
Ti	-0.37484	1							0.767848
Cr	-0.71472	0.399621	1						0.5786
Mn	0.975811	-0.22363	-0.73447	1					-0.74243
Fe	-0.84387	0.802008	0.654688	-0.74139	1				0.988631
Zn	0.481358	-0.71142	-0.72206	0.426758	-0.69403	1			-0.63609
Rb	-0.85227	0.49161	0.856817	-0.85221	0.810417	-0.69558	1		0.759753
Sr	0.152289	0.070219	-0.34983	0.243287	0.198569	0.069537	-0.30214	1	0.320848
Pb	-0.06352	-0.69799	0.103171	-0.20084	-0.42098	0.383873	-0.10537	-0.26748	-0.42698

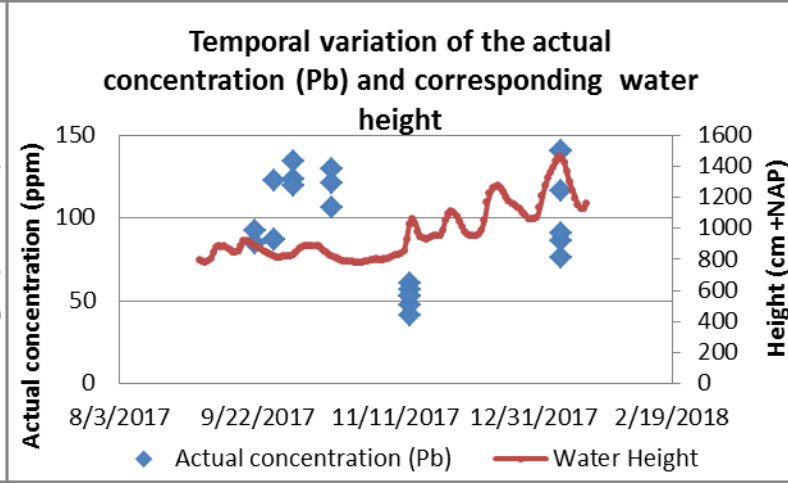
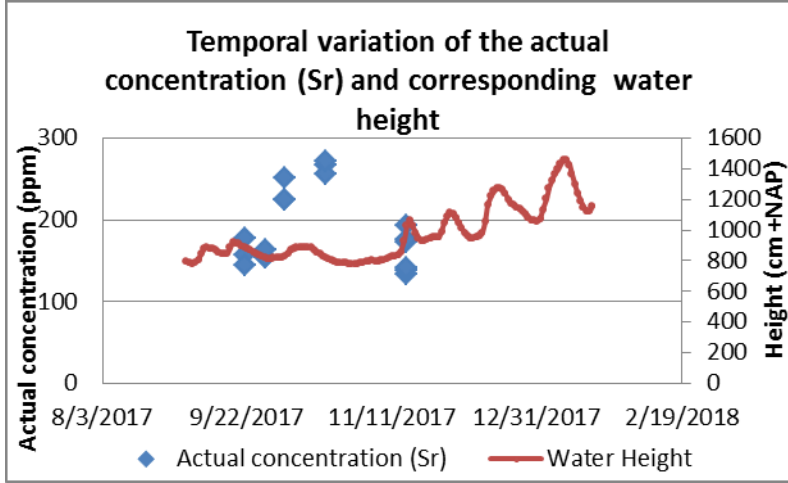
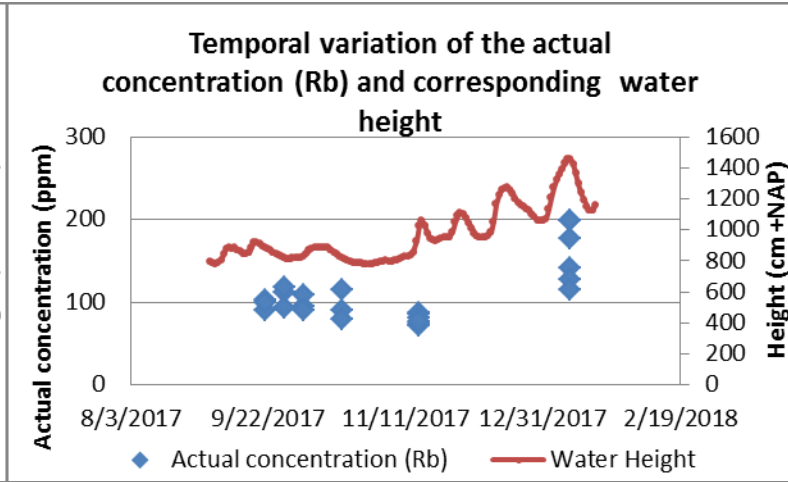
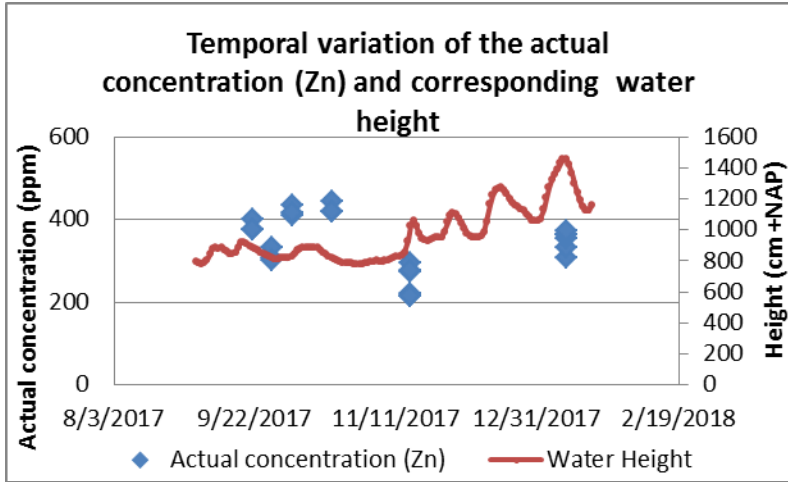
Correlation Oudendijk

	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Rb	Sr	h
Ca	1									-0.78557
Ti	0.218836	1								0.11343
Cr	-0.44939	0.424965	1							0.381594
Mn	0.905678	0.492943	-0.19079	1						-0.68576
Fe	-0.56592	0.581628	0.632181	-0.35482	1					0.799924
Cu	-0.59646	-0.53778	0.362272	-0.36788	-0.6146	1				-0.34419
Zn	0.795425	0.39059	-0.12191	0.888037	-0.44798	0.139546	1			-0.84923
Rb	-0.584	0.481928	-0.12191	-0.30522	0.777257	0.097076	-0.26955	1		0.561553
Sr	0.567932	0.447202	-0.42657	0.433374	0.353006	-0.72976	0.128045	-0.52696	1	0.057499
Pb	0.031691	0.636918	0.63189	0.325122	0.348686	0.020229	0.432386	0.521915	0.128992	-0.0723

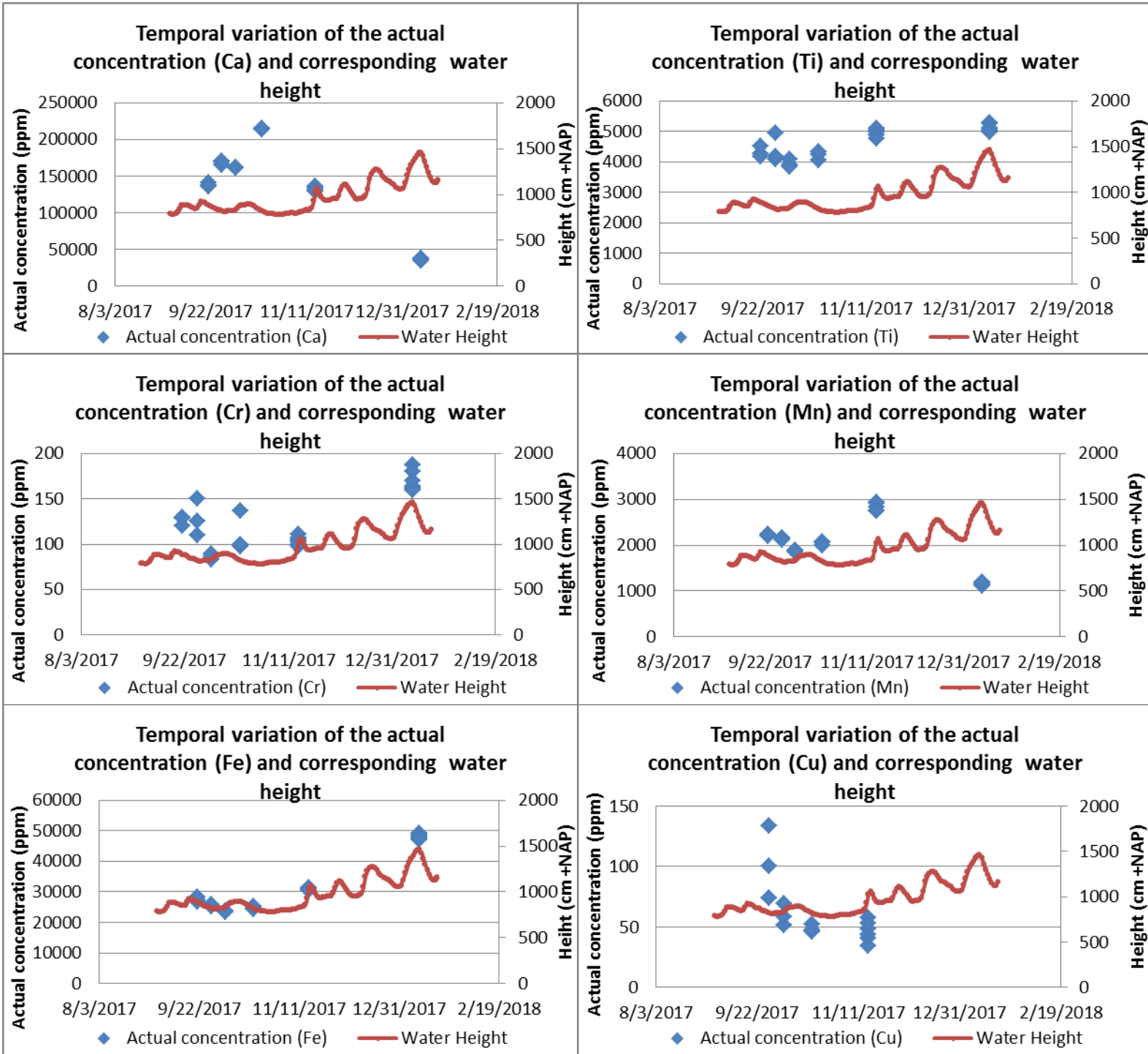
Appendix E: Temporal variation of element concentrations for sample locations along the Dutch part of the Rhine

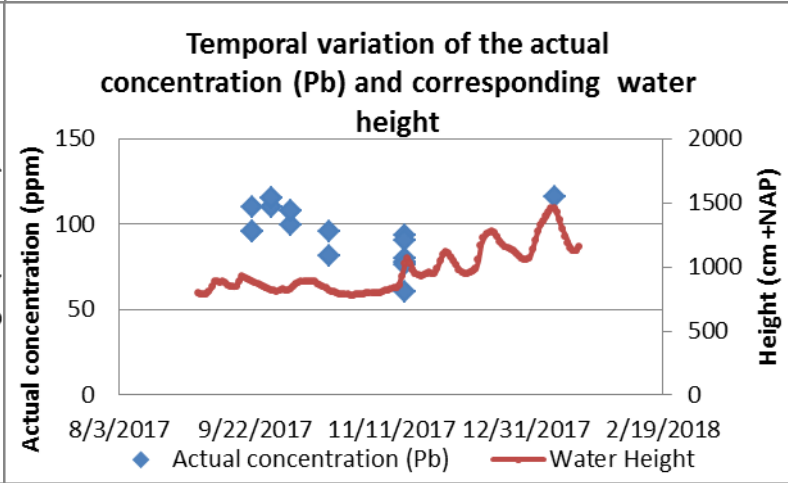
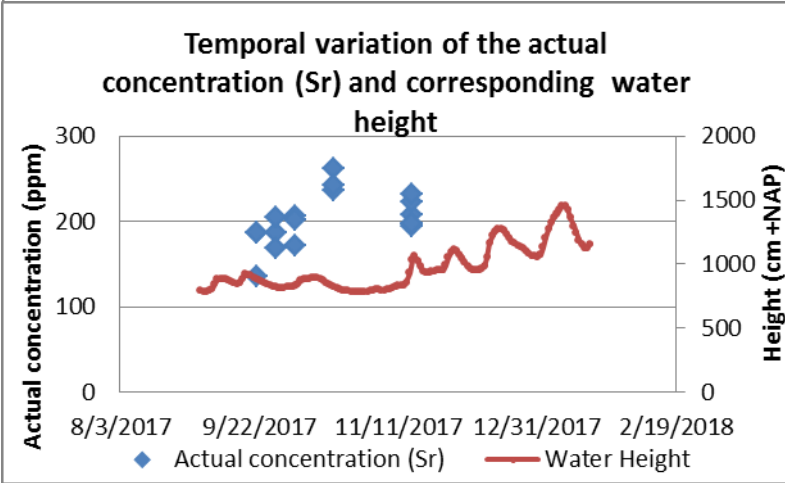
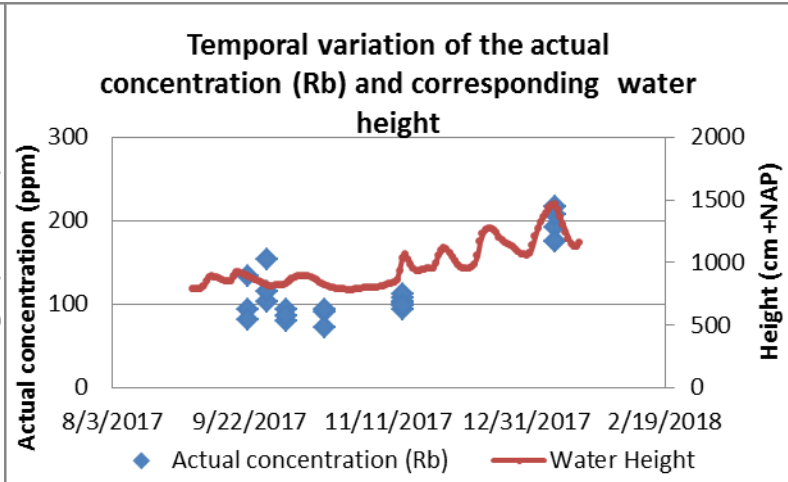
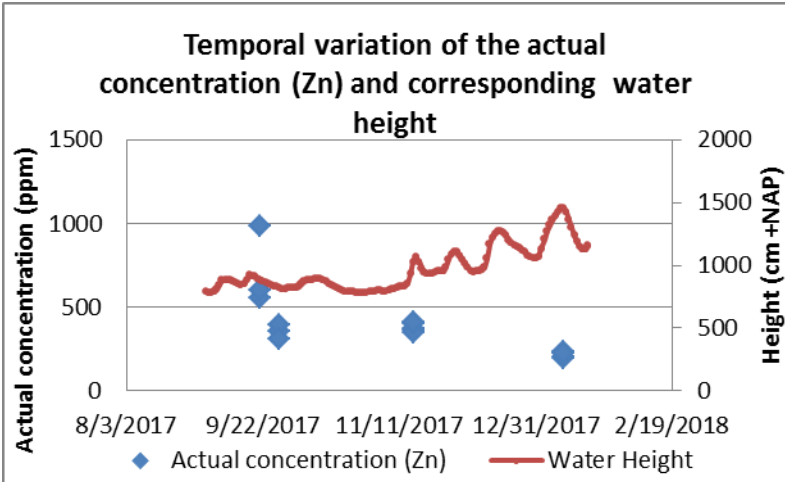
Ooij





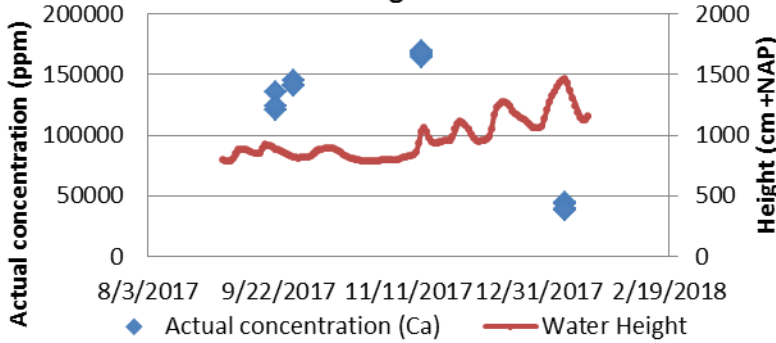
Wamel



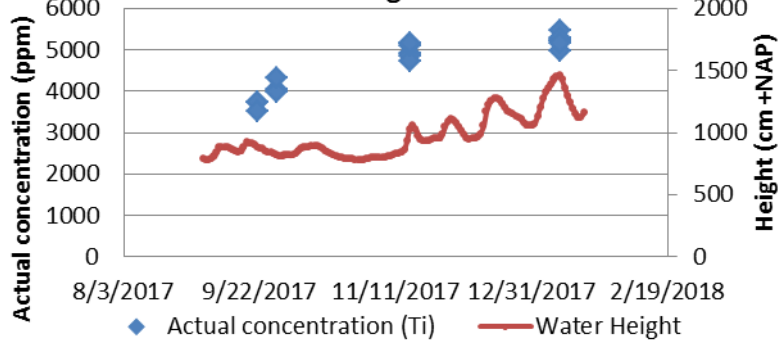


Vuren

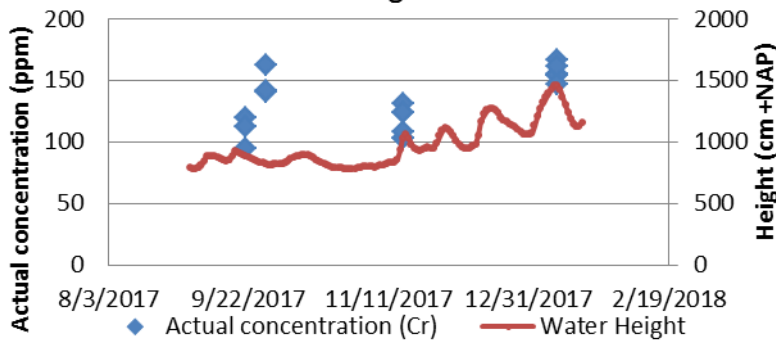
Temporal variation of the actual concentration (Ca) and corresponding water height



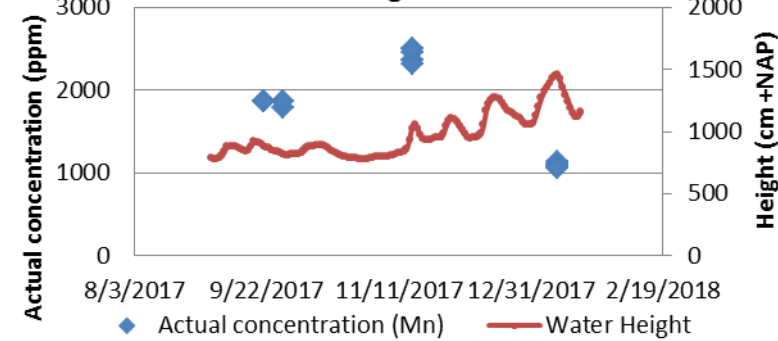
Temporal variation of the actual concentration (Ti) and corresponding water height



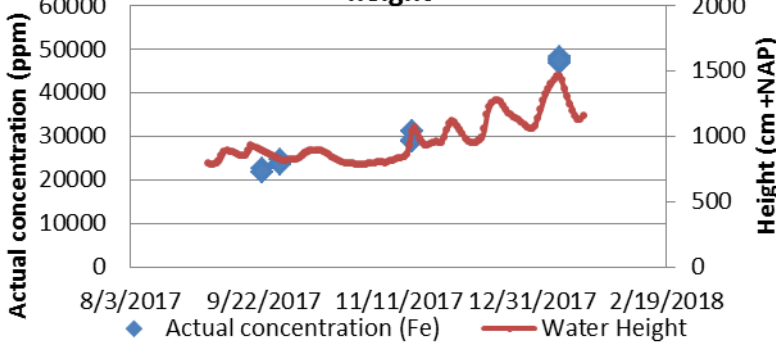
Temporal variation of the actual concentration (Cr) and corresponding water height



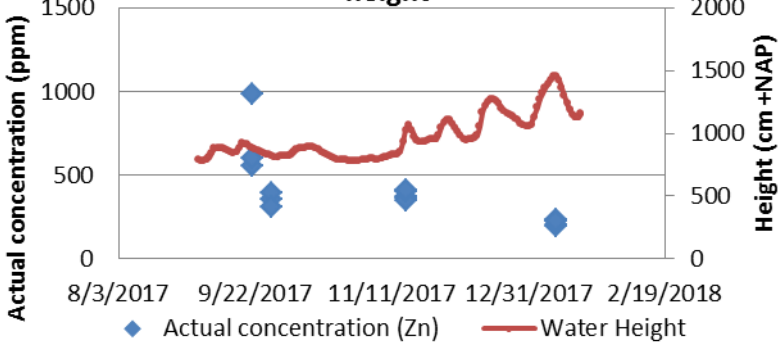
Temporal variation of the actual concentration (Mn) and corresponding water height



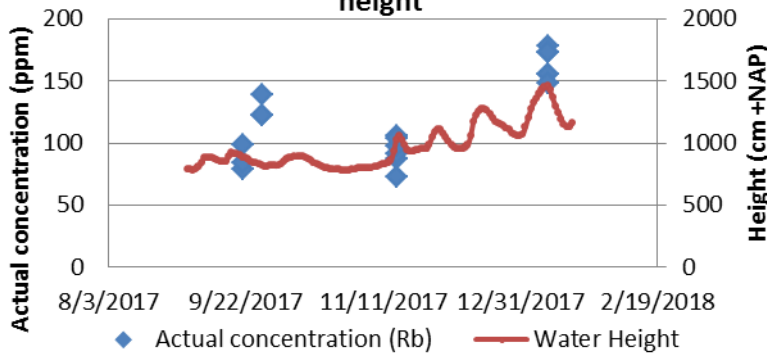
Temporal variation of the actual concentration (Fe) and corresponding water height



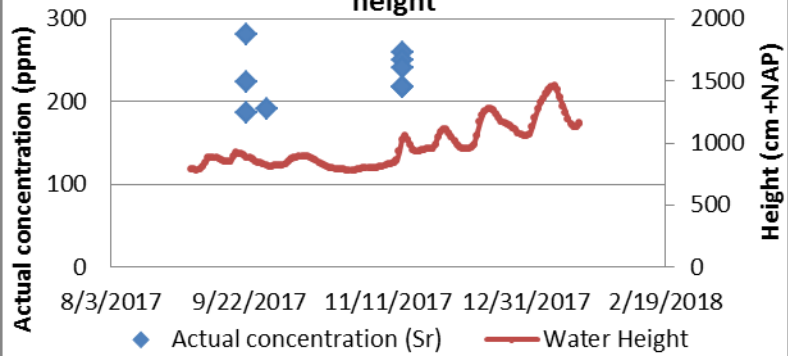
Temporal variation of the actual concentration (Zn) and corresponding water height



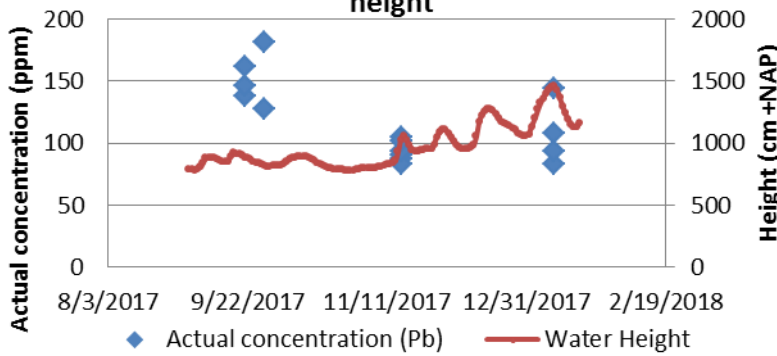
Temporal variation of the actual concentration (Rb) and corresponding water height



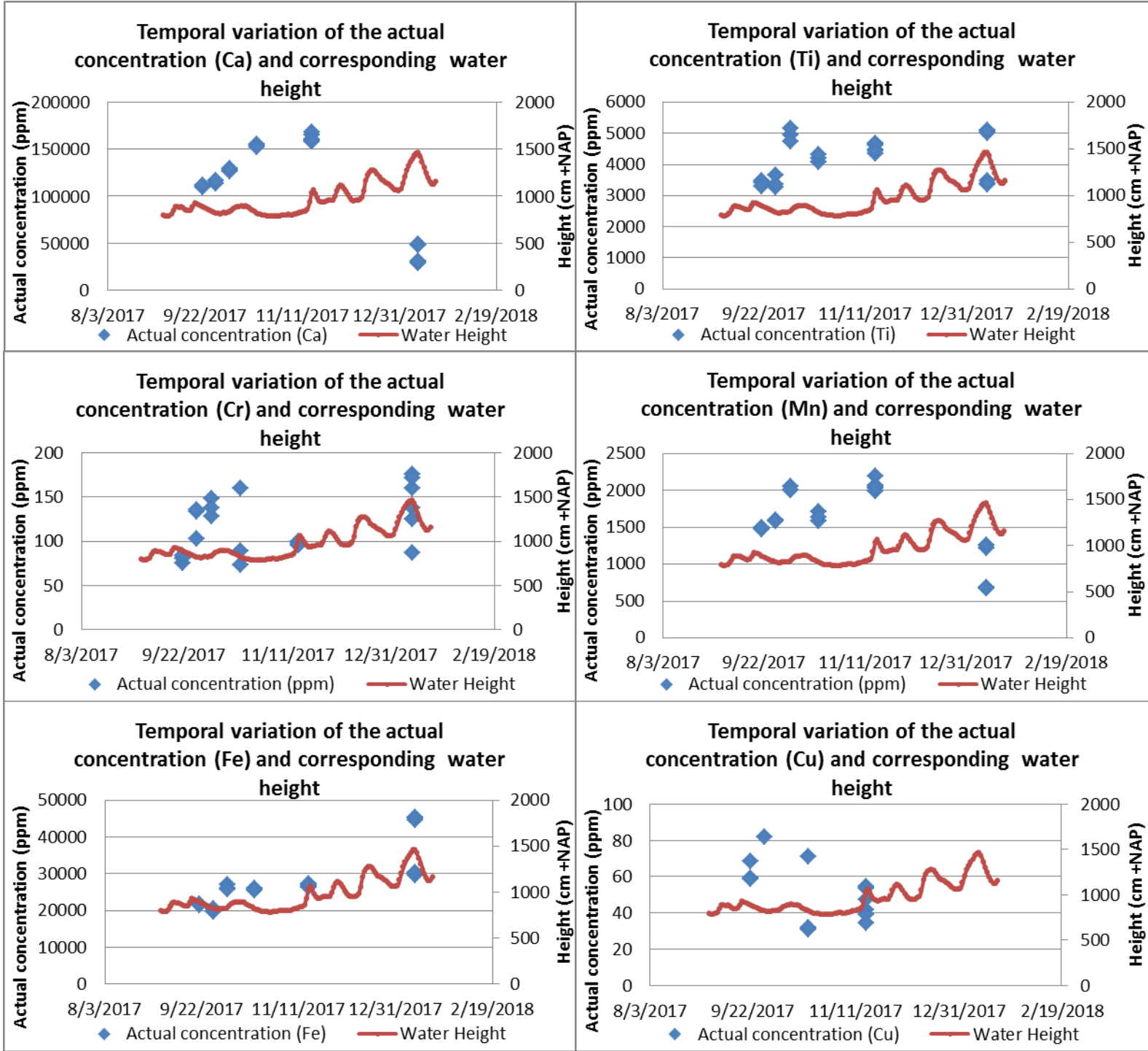
Temporal variation of the actual concentration (Sr) and corresponding water height

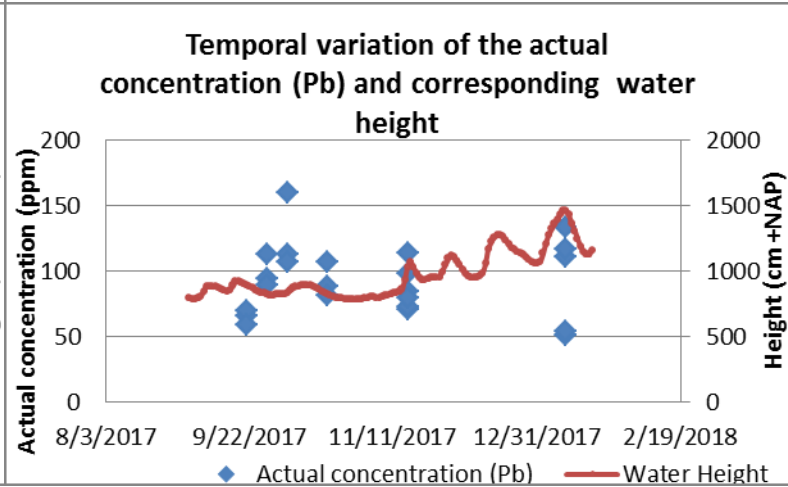
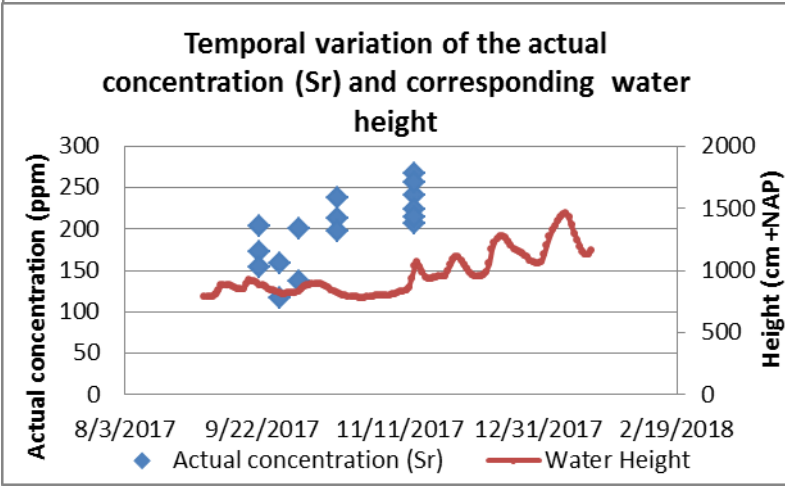
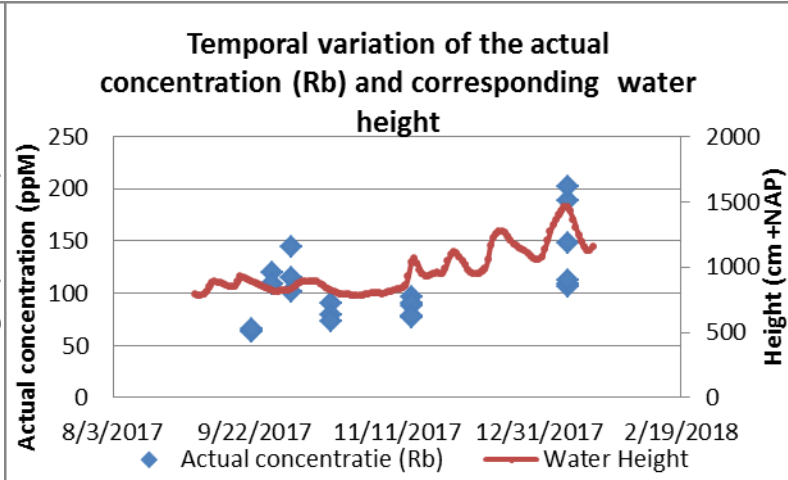
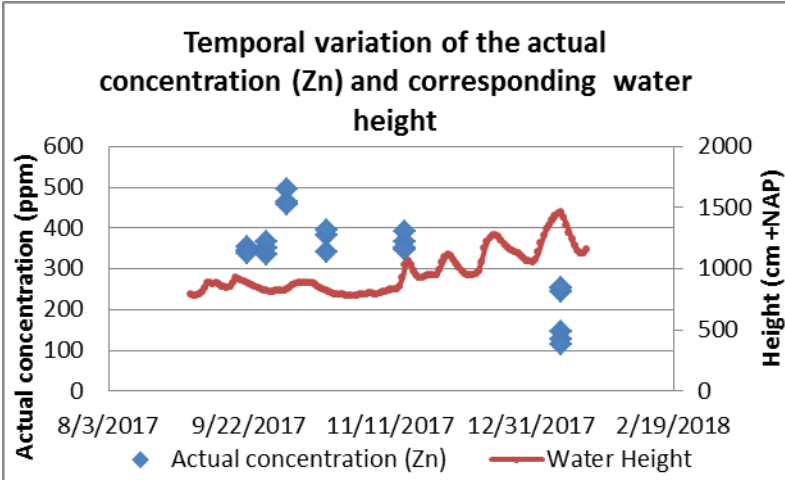


Temporal variation of the actual concentration (Pb) and corresponding water height



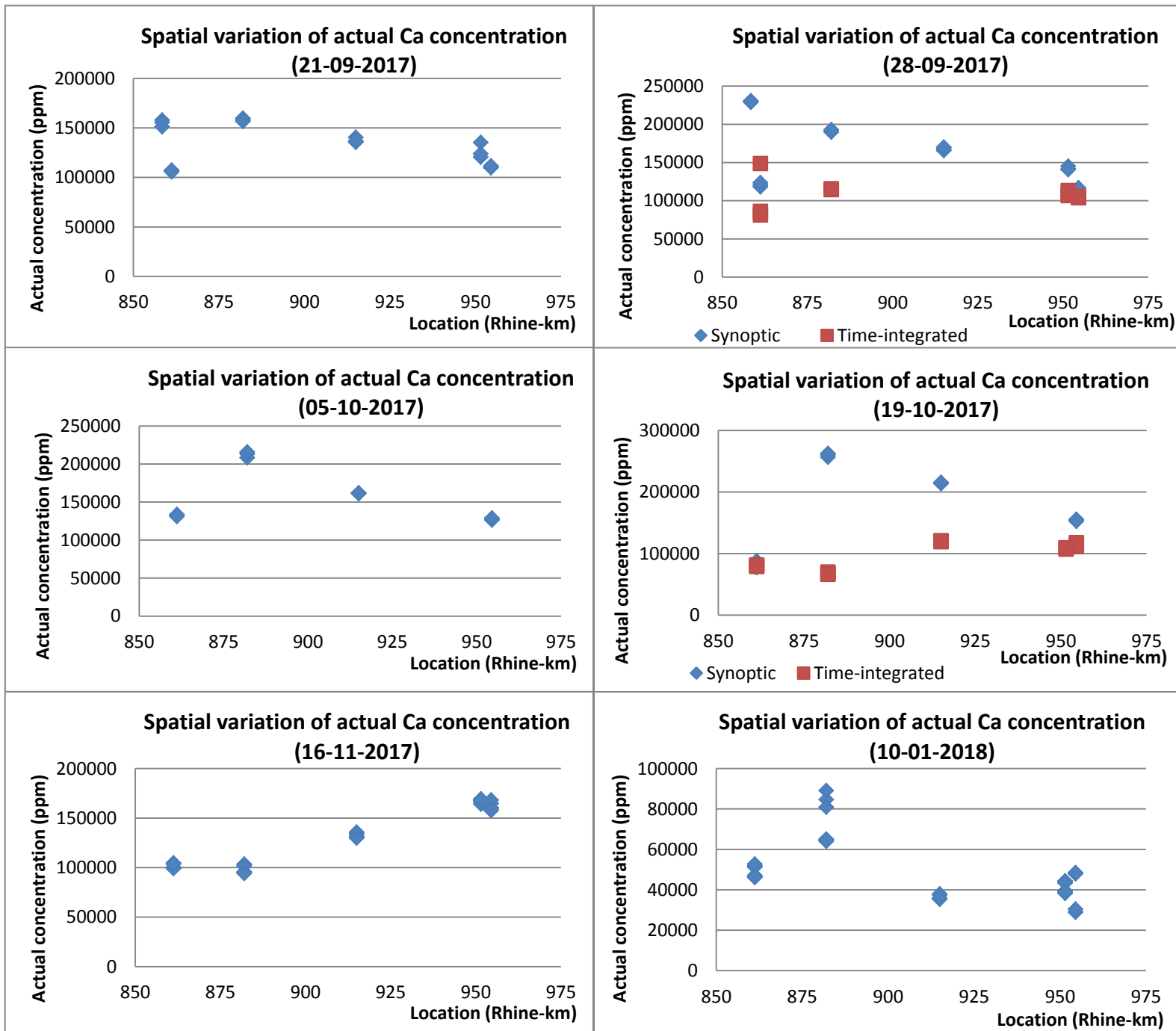
Oudendijk



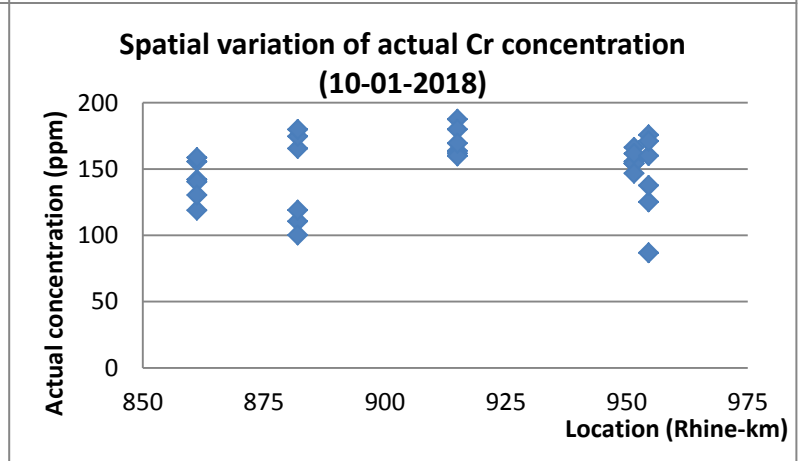
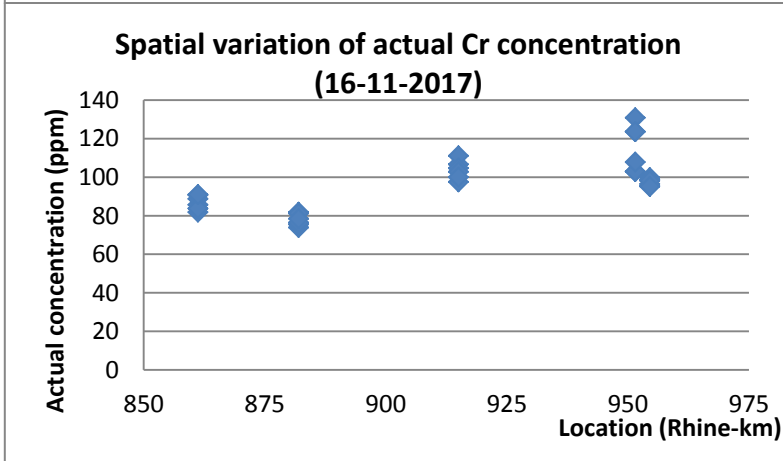
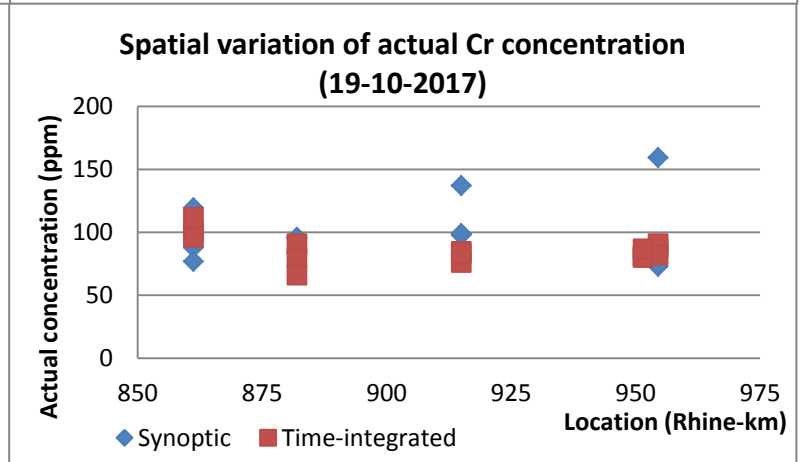
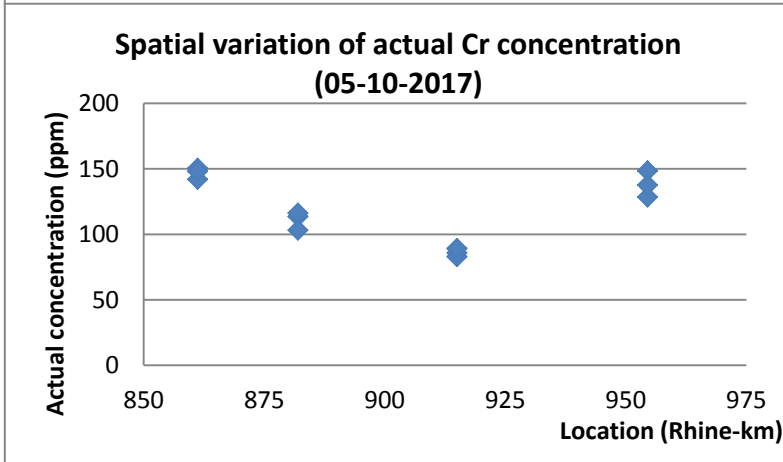
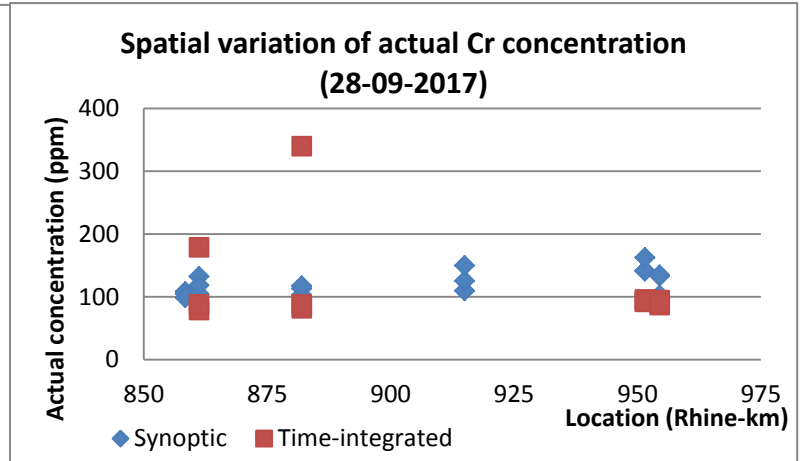
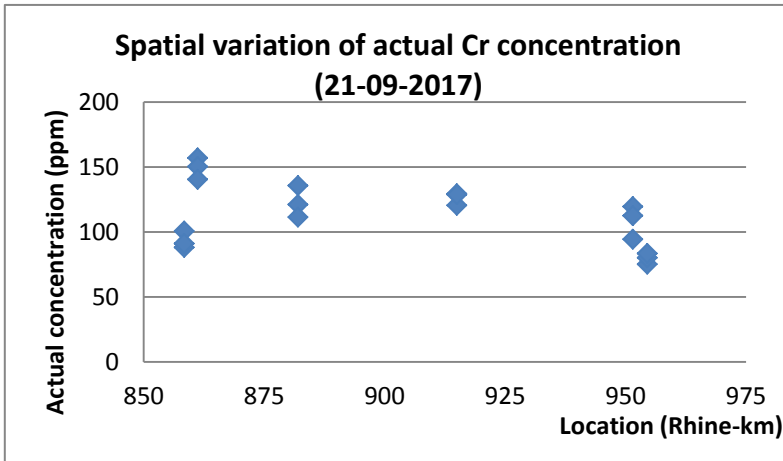


Appendix F: Spatial variation of element concentrations along the Dutch part of the Rhine

Calcium

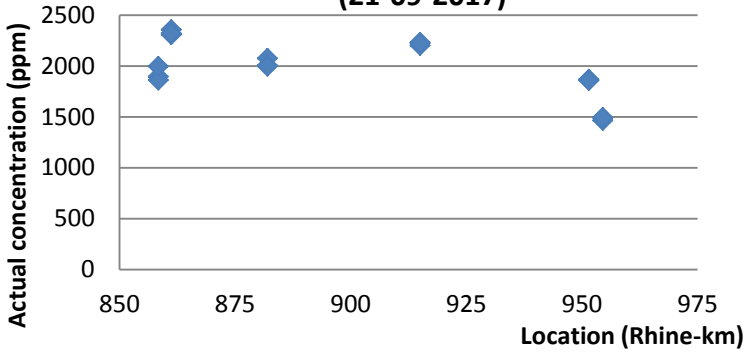


Chromium

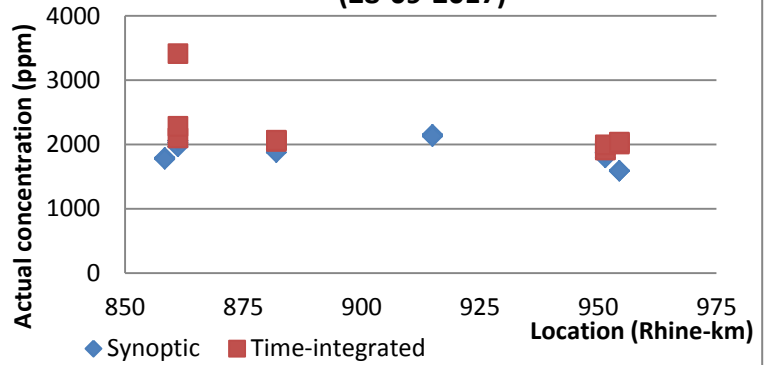


Manganese

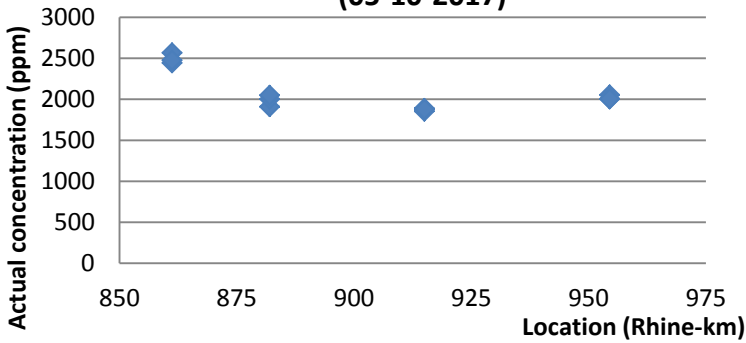
**Spatial variation of actual Mn concentration
(21-09-2017)**



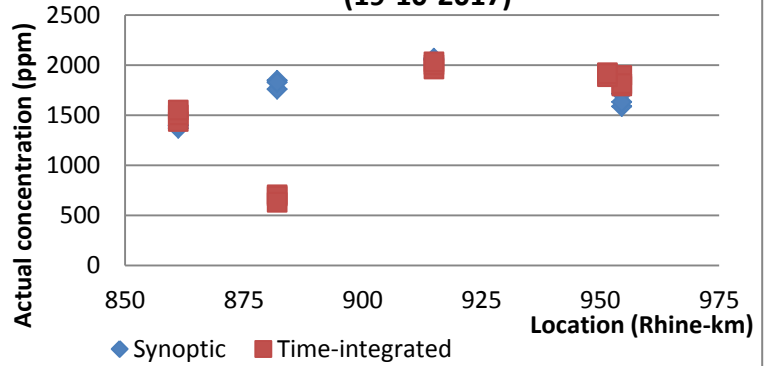
**Spatial variation of actual Mn concentration
(28-09-2017)**



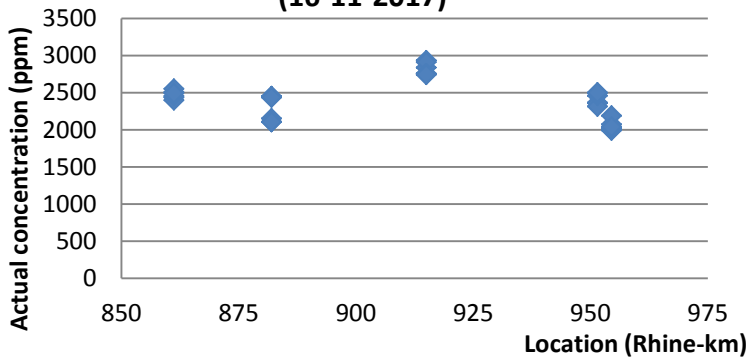
**Spatial variation of actual Mn concentration
(05-10-2017)**



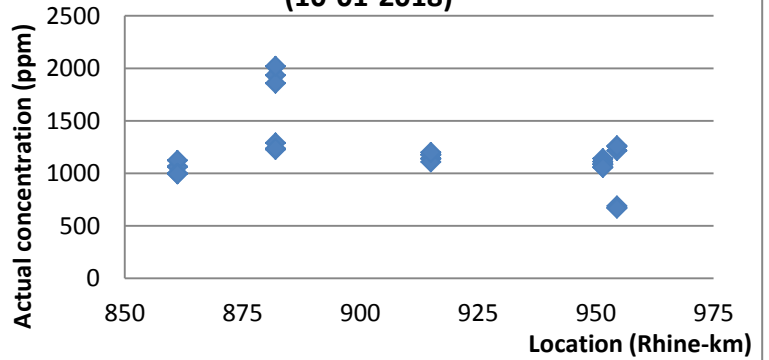
**Spatial variation of actual Mn concentration
(19-10-2017)**



**Spatial variation of actual Mn concentration
(16-11-2017)**

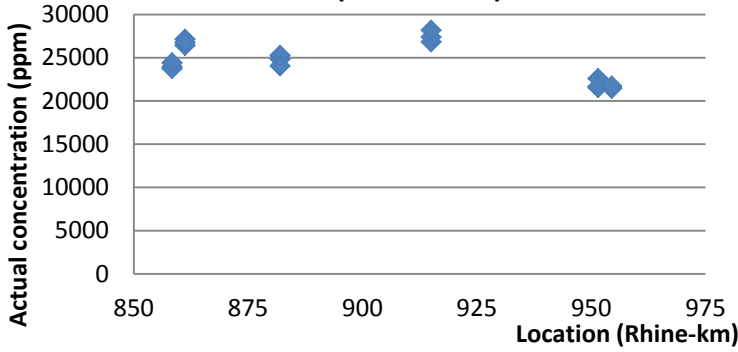


**Spatial variation of actual Mn concentration
(10-01-2018)**

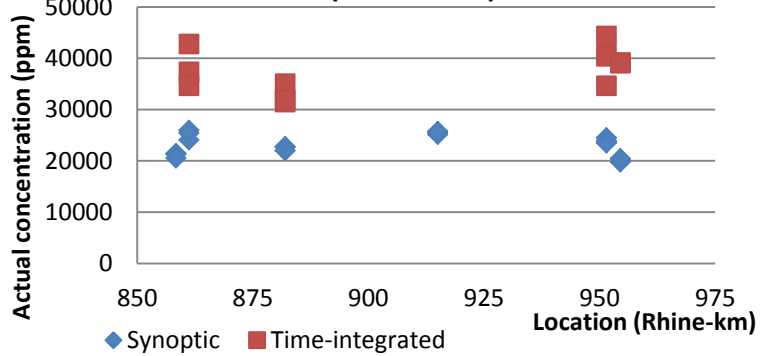


Iron

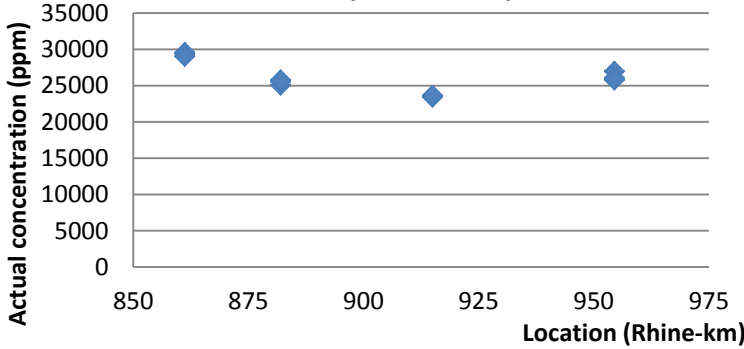
Spatial variation of actual Fe concentration (21-09-2017)



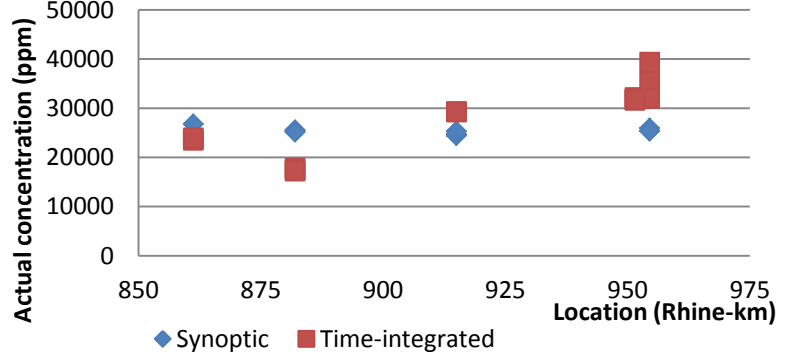
Spatial variation of actual Fe concentration (28-09-2017)



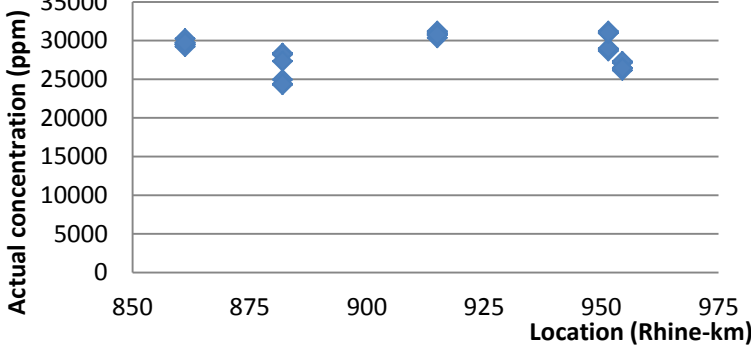
Spatial variation of actual Fe concentration (05-10-2017)



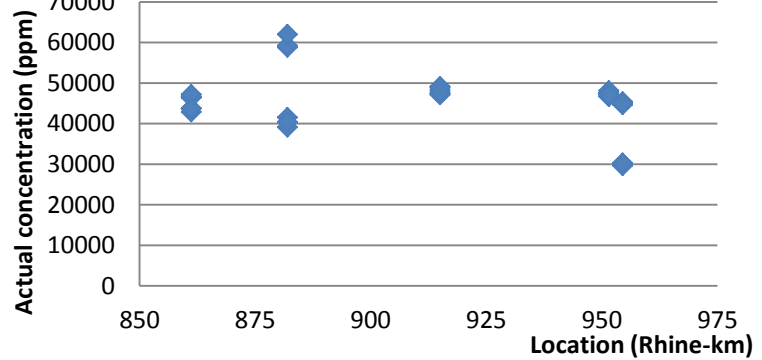
Spatial variation of actual Fe concentration (19-10-2017)



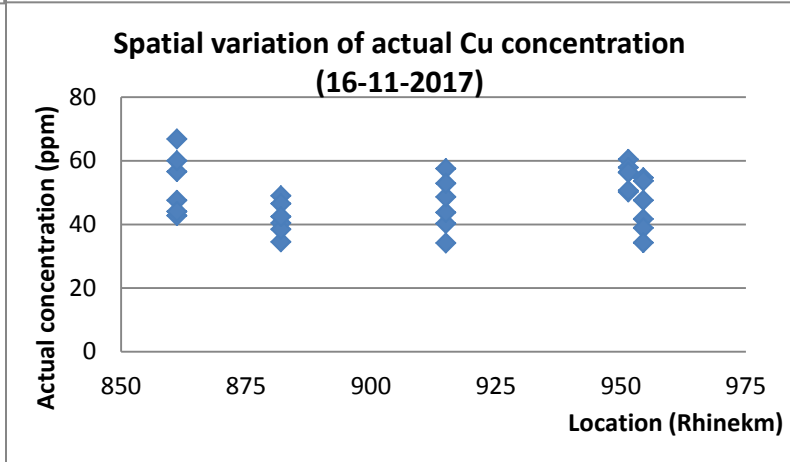
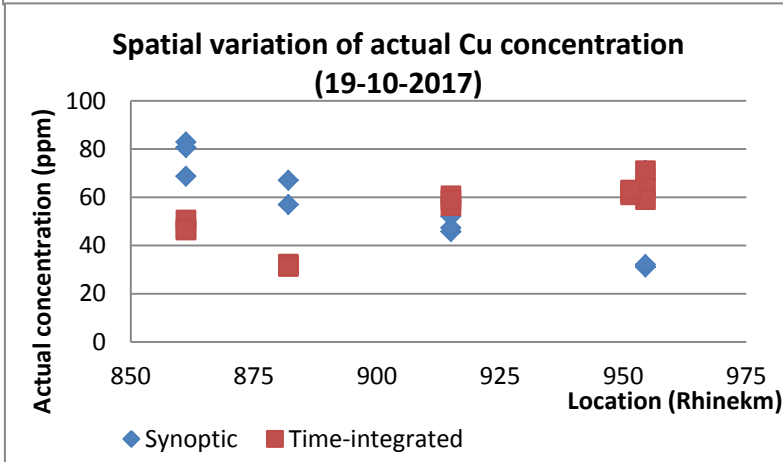
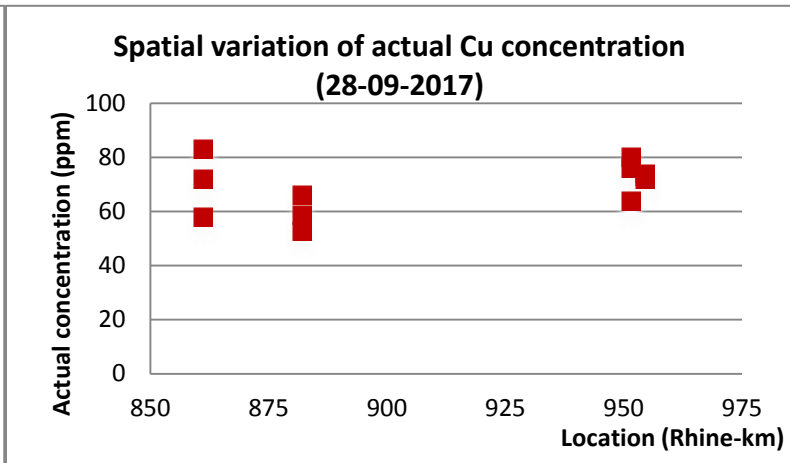
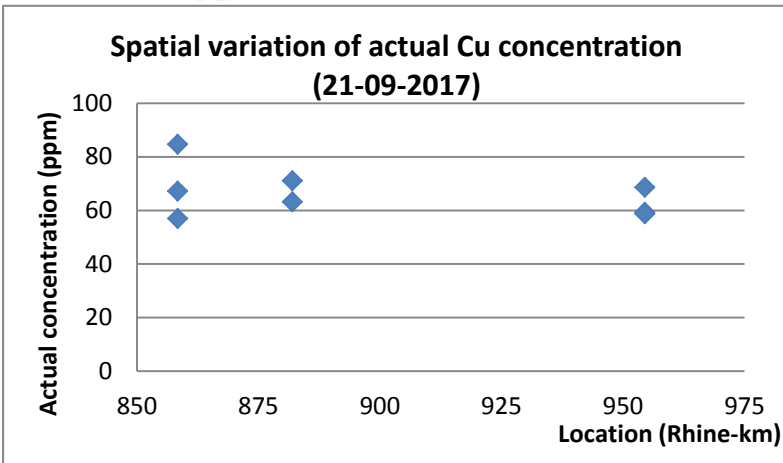
Spatial variation of actual Fe concentration (16-11-2017)



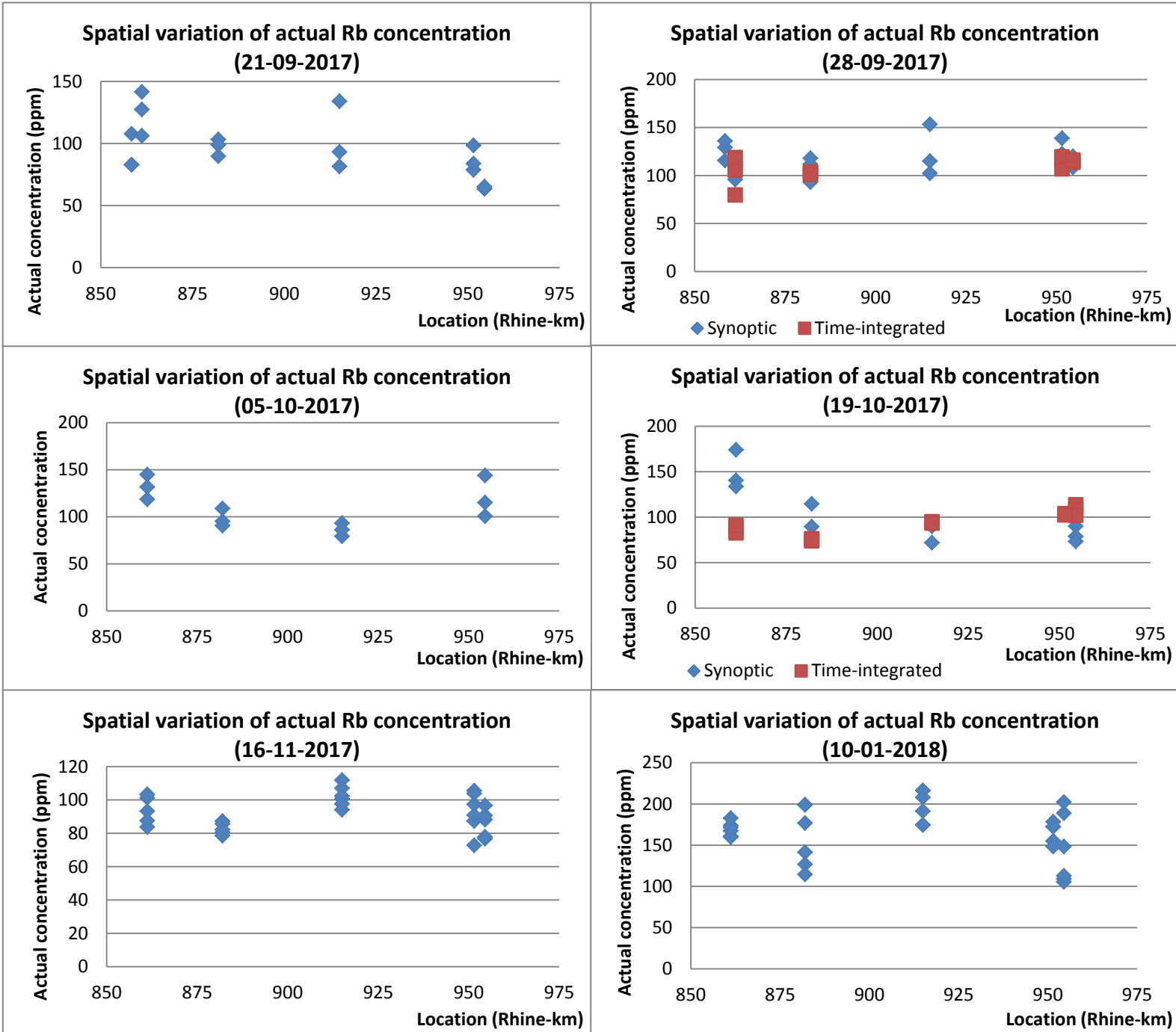
Spatial variation of actual Fe concentration (10-01-2018)



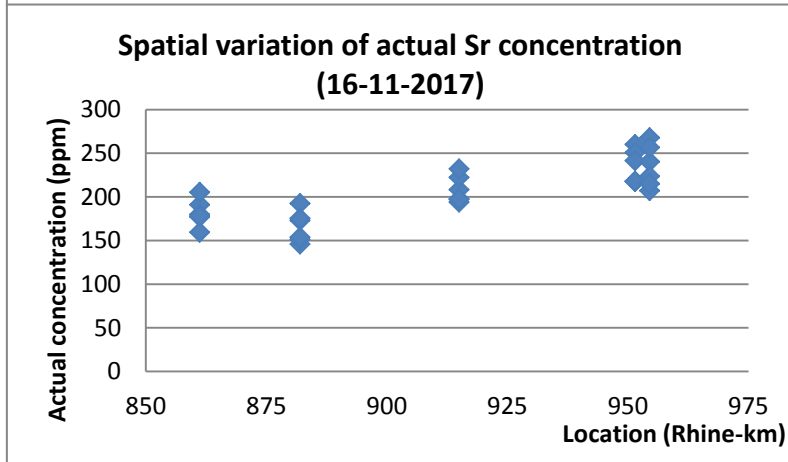
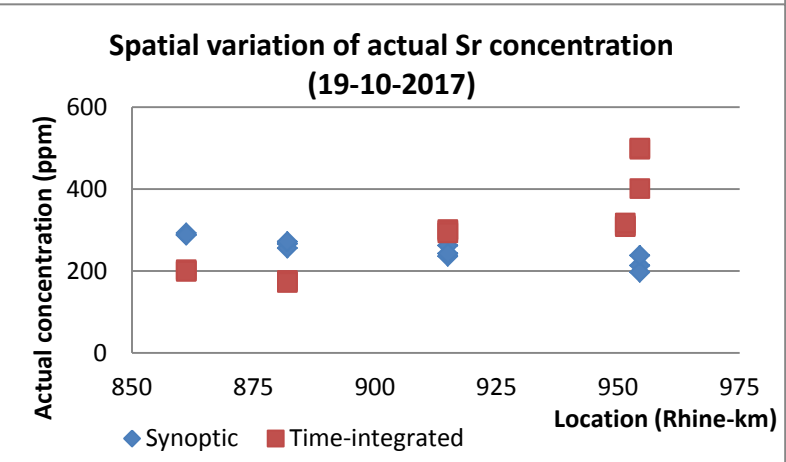
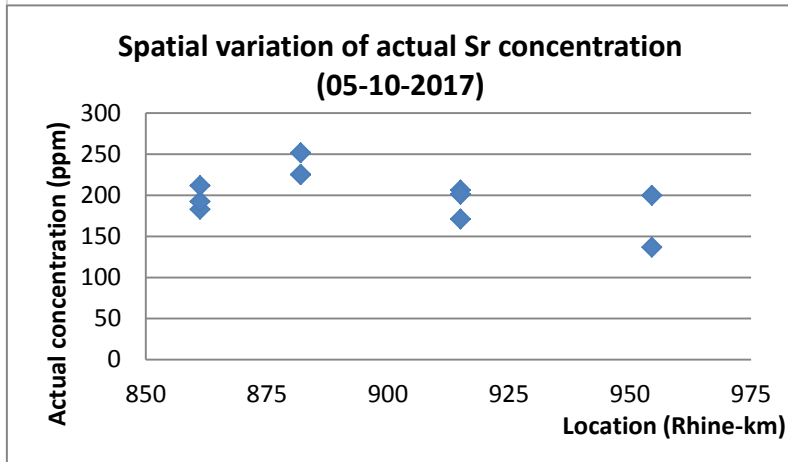
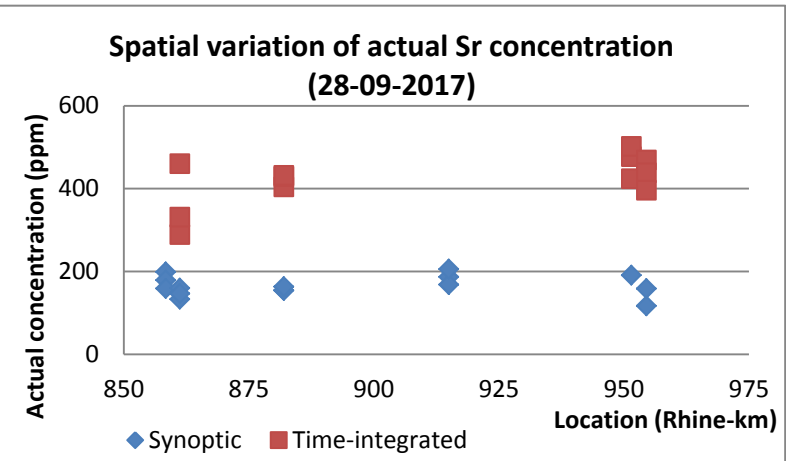
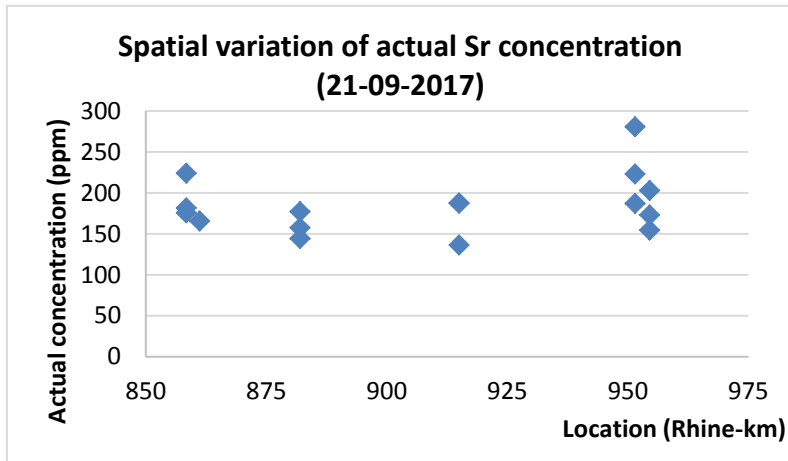
Copper



Rubidium



Strontium



Lead

