Diffuse phosphorus input to surface waters
- new concepts in removal, recycling and management -

P-TRAP – 1st Progress Report

Period: 1 March 2019 – 29 February 2020

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D5.8 P-TRAP – 1st Progress Report

Table of contents

Overview ESRs

ESR	Name	Title of project	WPs involved
1	Xingyu Liu	Develop a P-TRAP system to intercept the P flux from a drained catchment area into a recreational lake	**WP2**, WP3
2	Rochelle Saracanlao	Effect of applying vivianite and P-containing Fe(III) oxides on P bioavailability and dynamics in different agricultural soil types	**WP1**, WP3
3	Victoria Barcala	Improving the management of surface waters draining agricultural areas to optimize the retention and recovery of Fe-associated P	**WP1**, WP3
4	Oleksandr Bolielyi	Converting Fe residual materials into filter-stable sorbent materials for P removal	**WP1**, WP3
5	Lordina Eshun	Microbial technologies for converting P- loaded Fe (III) oxides	**WP1**, WP3
6	Mingkai Ma	Processes controlling P dynamics upon reductive transformation of P containing Fe minerals	WP2, **WP3**
7	Ville Nenonen	Mechanistic studies on the transformation of P-containing Fe(III)oxides	WP1, **WP3**
8	Tolulope Ayeyemi	The effectiveness of vivianite as a sustainable Fe and P fertilizer for agricultural crops	**WP1**, WP3
9	Karel As	Studying the effect of Fe addition to sediments on the sedimentary biogeochemical processes	**WP2**, WP3
10	Rouven Metz	Biogeochemical mechanisms influencing the bioavailability of P and Fe from vivianite	**WP1**, WP3
11	Melanie Münch	Effects of Fe supplementation on the ecology and P dynamics in eutrophic lakes	**WP2**, WP3

1. General Progress of P-TRAP

Within the 1st reporting period (1 March 2019 – 28 February 2020), the consortium of P-TRAP focussed on I) the recruitment of the 11 Early Stage Researchers (ESRs) and their training at the host institutions, and II) on first scientific activities. Within the scientific and training WPs 1 – 4, no significant deviations from the initial work plan were made.

Initially all ESRs started between project months 7 and 11 (September 2019 – January 2020). Unfortunately, one position had to be re-opened as the initially hired ESR unexpectedly quit. The new ESR was selected end of January 2020 and planned to start in March 2020.

Prior to the start of the ESR projects, the PIs started to discuss possible collaborations and synergies arising from the use of consistent sets of protocols, samples, and analytical tools. The ESRs spent their first months to familiarize with their study topics, experimental design and first laboratory work. The ESRs got acquainted with their new scientific environment, and also interacted among each other through Skype calls. Work in the first month of their research mostly involved reading, writing detailed research plans, and receiving first (instrumental, methodological) training at their host institutions. So far, the project is on track. Major experimental advances are expected for the second project year, as the ESRs become productive in their laboratory work.

In project month 11 (January 2020) the first network training event took place – TSTC1: Being a scientist in the 21th century. 9 out of 11 ESRs participated in the three days. TSTC1 has been reported as deliverable D4.1.

1.1 Work packages

1.1.1 Work Package 1 - Closing the cycle of P application in agriculture

WP1 is led by UNIVIE. All ESRs are contributing to different amounts to this work package. ESRs related to WP1 do interact on various levels, including person-to-person exchange and conference calls. The intensity of interactions on each level depend on the scientific or technical needs involved in working towards milestones and deliverables. An important element in WP management are the in-person meetings at annual meeting and training events. So far, the communication structure worked well.

1.1.1.1 Executive summary WP1

Work Package 1 (WP1) is concerned with developing an agricultural phosphorous recycling strategy including recovery of P leaking from agricultural soils, transformation of the recovered P into fertilizers and soil conditioners and demonstration of the suitability of these products for agriculture.

Specifically, ESR1 and 4 are concerned with developing a cartridge-based phosphorous trapping system (P-TRAP system) that can be applied in drained agricultural. The P-Trap system will be developed and tested in field sites (ESR3) and quantitative models will be developed to enable predictions of their performance (ESR3, 9). Long term performance of Fe-containing sorbents in drainage systems will be investigated at test sites at which P retention based on Fe sorbents have been investigated in the past by DELTARES and other research institutions (ESR6, 7)

New microbial technologies will be developed for converting P-loaded Fe(III) oxides into vivianite and other products of higher economical value (ESR5, 6, 8). The effect of their application to agricultural soils is in investigated by ESR2, 8 and 10.

So far, work related to WP1 is on track as described in more detail in Chapter 1.1.1.3.

1.1.1.2 Progress summary per WP partner

All beneficiaries are involved in WP 1. At **UU**, ESR6 has started to design and perform experiments to determine the release of P upon the reaction of Fe oxides, which are initially binding P, with sulphide. As an experimental approach, it was decided to use flow-through reactors, which allow determining the progress of the reaction at controlled conditions. The experimental set-up has been developed and first tests have been performed, including break through curves using inert electrolyte solutions and first experiments with iron oxides in the reactor and sulphide in the inflow solutions. The analytical procedures for determining dissolved sulphide, Fe and P in the out flow have been tested. For the first experiments, lepidocrocite (gamma-FeOOH) was used, which forms in natural environments upon the oxidation of Fe^{2+} containing solutions. Adsorption of P to lepidocrocite has been investigated and first reactor experiments with lepidocrocite with adsorbed P are currently being performed. Additionally, methods for characterizing Fe containing solids are currently being tested. This includes FTIR, Raman spectroscopy, XRD, and electron microscopy.

UNIVIE is involved in Task 4, where the effect of Fe and P containing phases on soil fertility and quality will be investigated. In order to provide well characterized vivianite as a standard material, to which the effect of less well-defined vivianite-containing fertilizers or soil conditioners can be compared, ESR10 started efforts to set up vivianite synthesis protocols.

Different batches of vivianite were synthesized with varying synthesis parameters. Attempts were made to produce minimally oxidized vivianite by modifying standard protocols, and also to obtain different particle sizes and, hence, surface areas to compare the reactivity. The synthesized vivianite has been characterized using for its mineralogy (X-ray diffraction, Raman), surface area (BET), particle size, and Fe(II)/Fe(total) ratio (photometry).

EAWAG contributes to phase characterization of P-containing Fe(III) oxides. This includes naturally formed Fe-associated P from drainage systems (Task 2) and microbial conversion educts and products such as vivianite and other soil fertilizers or conditioners (Task 3). As these materials have not been sampled or synthesized at this stage, ESR7 did not produce results of direct relevance for these tasks. However, ESR7 has done significant work in transformation and analysis of P-containing Fe(III) oxides as detailed in the WP3 report. Also, different types of water treatment residues (Fe-oxide sludges, pelletized Fe-oxide sludge, Fe-oxide coated sands) were obtained from AquaMinerals and are currently characterized for basic properties (elemental and mineralogical composition, specific surface area) as a basis for continuing work on the structure and reactivity of these solids relevant to P-TRAP systems. The experiences gained in this work is prerequisite for the input of ESR7 to Tasks 2 and 3.

Until February 2020 different vivianites have been synthesized by **US** for the study of their solubility and potential release of P and Fe (in collaboration with ESR2). In February 2020, we start experiments with synthetic vivianites that differ in elemental composition (P content, Zn and Mg incorporation) to assess their solubility and effect on P uptake by plants in artificial growing media, as a first approach to the study of the P fertilizer effect of vivianite from different origins. The experiment, involving cucumber cultivation in pots, is performed using calcareous sand mixed with siliceous sand as growing media to simulate a calcareous soil where the precipitation of Ca phosphates is the main process constraining the efficiency of P fertilizers. The main variable to be studied will be P uptake by crop, and apparent recovery of applied P fertilizers. Comparison with a control with soluble mineral fertilizer will be done. Despite the application of Fe, Mn, Zn, and Mg in the nutrient solution, the potential effect of the different vivianites on these nutrients will be also assessed.

While it was initially expected that **KUL** has field stations for the observation of P and Fe export of drained agricultural areas, the access to these sites is not available anymore. Therefore, they will not contribute to Task 1 and 2 as planned initially. However, KUL has a significant role in the investigation of the applicability of P and Fe as soil conditioners. In this context, a large effort was put into the compilation of extraction procedures for the characterization of solid-phase P and Fe in soils and sediments to be used within P-TRAP (milestone MS5). Protocols for the extraction of P and Fe from soils were mainly contributed by KUL and US, respectively. UU contributed the standard procedures for the extraction and analysis of different fractions of P and Fe from sedimentscomment on MS5.

In the context of research on converting Fe residual materials into filter-stable sorbent materials for P removal, **GEOS** started a study on the raw material properties. Samples of Schwertmannite were collected from the pilot plant in Tzschelln and another sample was kept in GEOS for some time (not specified). All studies yet were carried out with the model solution of P. Till now the data about the moisture content, adsorption capacity and kinetical parameters of raw Schwertmannite were obtained. The data obtained confirms that there is aging effect towards adsorption of Phosphorus on Schwertmannite. Maximum adsorption capacity remains unreachable. Research continues as the Schwertmannite has potential to be as an additional compound, which can later be applied for P-binding in lake sediments.

Deltares started to investigate how particles with Fe-bound P are transported. To answer this question sediment transport will be studied at two different scales. For the large scale, river sediments will be sampled and for the smaller scale one farm draining to one exclusive ditch will be investigated. First investigations have been made on the farm scale at a project location of a running Deltares project. ESR3 started also working on building a Fe map of shallow groundwater of the Netherlands and the correlation between Fe in groundwater and other ions such as SO_4, NO_3, Ca, Mg, Al, PO_4.

No scientific work related to WP3 has been performed by **UNIMAN** in the first project year due to delays associated with visa problems for ESR5. Current activities focus on preparing chemical and biological safety assessments. Laboratory experiments will be started from first week of March by growing *Geobacter sulfurreducens* and using cells of this Fe(III)-reducing bacterium to reduce synthetic Fe(III) oxides (ferrihydrite) and soluble Fe(III), in the presence and absence of phosphate, with the aim of synthesizing reference “biovivianite” materials. Subsequent experiments will be performed with sediments, soils, and waste materials in bioreactor systems. The obtained solids will be characterized with a broad range of techniques, including synchrotron X-ray based spectroscopies.

UBT has not contributed to WP1 yet as the initial ESR1 appointee, who started in October 2019, resigned due to personal reasons.

1.1.1.3 WP 1 – Task report

Task 1: Develop barrier systems (P-TRAP system) to retain and recover dissolved P in drainage systems (GEOS, UBT, KUL, UU)

> *Develop novel granular materials from Fe-containing by-products of water treatment, test the characteristics of these materials regarding P-binding, hydraulic properties and stability under field conditions, develop suitable carriers for these materials which can be employed in drained agricultural areas, test the performance of the P-TRAP system under field conditions.*

The work of ESR 6 contributed to Task 1 in this work package as well as to Task 1 in WP 3 in view of the long-term retention of adsorbed P in the P-TRAP system. That is, ESR6 investigates the fate of P, which is adsorbed onto Fe(III)-oxides, when reducing conditions develop. In particular, the release of P will be determined when sulphate reduction is induced in the P-TRAP system. The extent and kinetics of P release are investigated in flow-through reactor experiments, in which iron oxides containing adsorbed P are exposed to dissolved sulphide in the in-flow solution. First results indicate that the appearance of sulphide causes a release of adsorbed P, which is reflected in an increase in P concentrations in the out-flow (see Fig. 16 in Chapter 1.1.3.3). After the initial increase in P concentration, the concentrations decrease and reach a steady state. When the flow is interrupted for several hours, the resumption of the flow leads to an increase in P concentration in the out-flow. These results indicate that part of the adsorbed P is readily released when sulphide emerges in the solution. This release can be attributed to competitive adsorption of sulphide and P. However, not all adsorbed P is instantaneously released but part of the P is slowly released with a time scale of several hours. A possible reason for the split picture of P release and the development of a kinetic model to describe the P release dynamics and the relationship with sulphide composition and mineral transformation are objectives for future experiments and investigations.

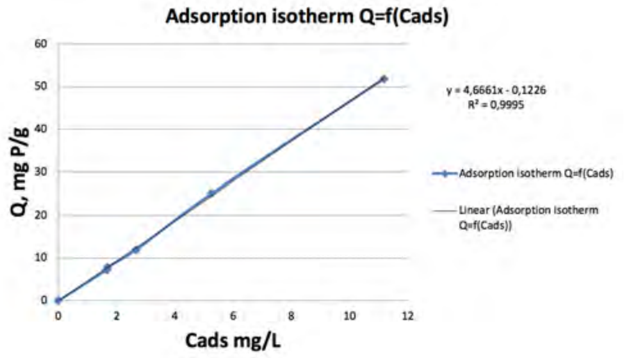

Fig. 1: Batch experiment adsorption isotherm

Kinetic experiments were carried out for more than 500 hours. A solution prepared from $Na_2HPO_4*H_2O$ with a concentration of ortho-P of 100 mg/L was used. The pH was adjusted to 7.5 using 0.1 M HCl. Aged Schwertmannite and fresh Schwertmannite collected from pilot plant in Tzschelln on 11th of December were used as sorbents. Fresh wet material was dried at 50°C. Approximate concentration of Schwertmannite used was 200 mg/l for dried material. Samples were placed into 500 ml bottles and were shaken constantly at 150 rpm. Samples were analysed every 24 hours photometrically with the use of Phosphate spectroquant tests (Merck, molybdenum blue method). Results confirmed, that fresh raw material has a higher adsorption capacity than aged material. Schwertmannite can remove up to 46 mg P per g of fresh schwertmannite (1.5 mmol P/g), while aged schwertmannite can remove up co 29 mg P/g (1 mmol P/g). The maximum adsorption capacity was not reached within 500 hours with concentration of 100mg P/L. During kinetic experiments pH slightly declined down to 7.2.

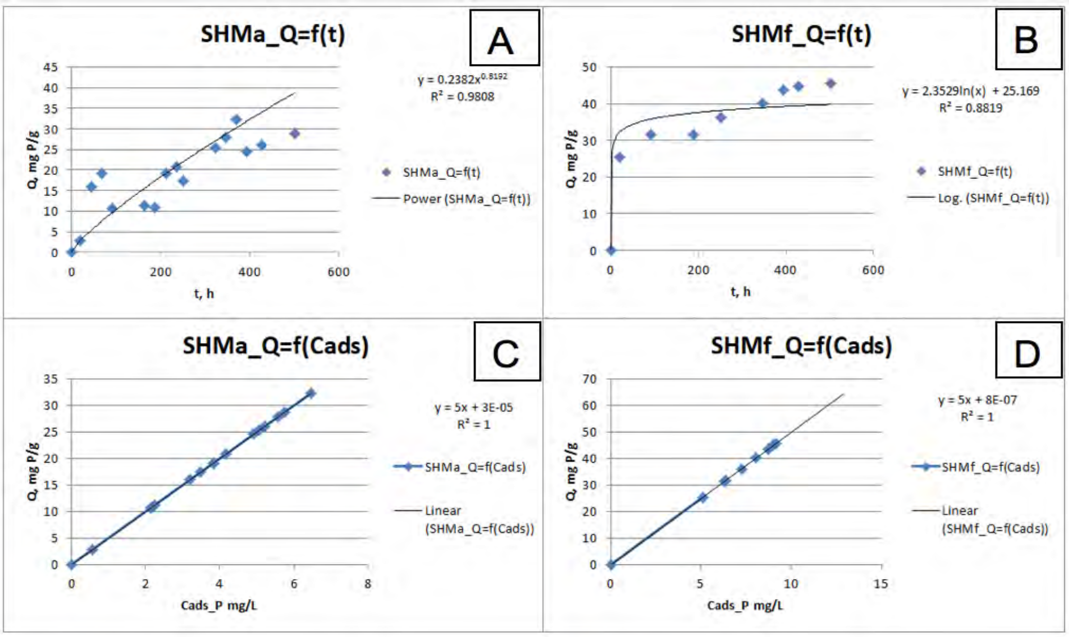

Fig. 2: A and B: Kinetic data of P adsorption on fresh or aged schwertmannite. (A) aged Schwertmannite; (B) fresh schwertmannite. C and D: Adsorption isotherms. (C) aged Schwertmannite; (D) fresh Schwertmannite.

Further research will be carried out with other raw materials such as iron sludge. We assume that mixtures of schwertmannite with other raw materials may lead to better agglomeration characteristics. There is an option to carry out experiments in acidic and alkaline media. Also, we consider carrying out experiments at higher total concentrations of P in order to investigate maximum adsorption capacities. However, this work would only contribute to a better understanding of the adsorption behaviour of P on schwertmannite. From a practical point of view, we don't expect corresponding high equilibrium concentrations of P in real surface waters.

In order to compare the efficiency of novel filter materials as to be developed in Task 1, ESR3 started to investigate two existing field sites where mitigation measures were already taken. Both sites are in drained agricultural fields. One site is the tulip area, this area has low Fe concentrations in groundwater and therefore the dissolved P is one of the highest in the country, here iron coated sand filters were implemented as a mitigation measure in some fields. Nevertheless, the P removal is not working as expected, one of the objectives in this field site is to understand why. The other site is a cattle farm, there is data from continuous monitoring of nutrients over the past year, mitigation measures will be implemented soon, so a detailed evaluation of the effect of the measures can be done. On this last farm samples were taken to analyse special changes in PO_4 and Fe concentration in the ditches.

Task 2: Develop approaches to optimise the retention and recovery of naturally formed, Fe-associated P in drainage systems (DELTARES, KUL, UBT, EAWAG)

> *Transport and transformation of naturally formed Fe-associated P in drained systems will be studied, opportunities of using hydraulic measures to retain Fe-associated P will be explored, possibilities to recover these P containing solids will be identified.*

The survey of groundwater quality with respect to Fe, P and other associated GW constituents by ESR3 will serve as an important information source for identification of sites in which naturally formed, Fe-associated P will be found for investigation in Task 2. Specifically, ESR3 is working on building a Fe map, of shallow groundwater of the Netherlands and the correlation between Fe in groundwater and other ions (SO4, NO3, Ca, Mg, Al, PO4) and other available data as: geology, soil type, land use, groundwater levels. To obtain these correlations machine learning techniques are being used. The correlation coefficients between these parameters and the Fe concentration in ground water is 0.75 using the whole database and the Random Forest Algorithm. The trend in the Fe concentration in groundwater given certain characteristics can be predicted. The map obtained so far is not continuous, it only has discrete data points. There are 62578 points from 0 to 30 m depth and 6871 points from 0 to 5 m depth. From these points we have the Fe information, the open source data, but information about the other ions is sometimes missing. No clear geographical regions with higher Fe were detected, high Fe values are scattered all over the country. Nevertheless, some trends can be detected, as higher values as depth increases, higher values in agricultural land use than natural land use.

Task 3: Development of microbial technology to converting P-containing Fe(III) oxides into vivianite and other soil fertilizers or conditioners (UNIMAN, EAWAG, UU, US)

> *Procedures, based on microbial reduction of Fe(III), will be tested and evaluated to convert P-containing Fe(III) oxides into vivianite and other products of potential value as fertilizer or soil conditioner.*

Preparatory work for Task 3 is under way by ESR5. So far, ESR5 focused on obtaining laboratory training and completion of chemical risk and safety assessments which are needed before any laboratory experiments could be initiated at UNIMAN. As part of the laboratory trainings, ESR5 had the opportunity to witness an on-going experiment where *Geobacter* was used to reduce synthesized ferrihydrite into biomagnetite.

Ongoing initial experiments focus on growing *Geobacter* cells and the cells of this Fe(III) reducing bacterium will be used to reduce Fe(III) oxide (Fe citrate-soluble) with and without the presence of phosphate. Biovivianite will be produced especially in experiments containing phosphates.

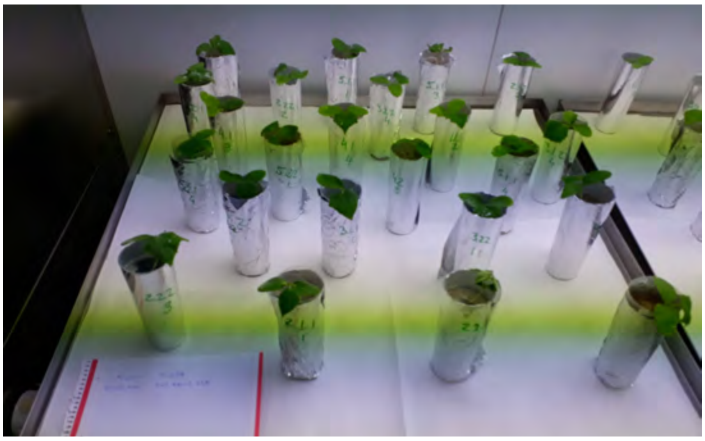

Fig. 3: Growth experiment using cucumber seeds on different vivianite products

Ferrihydrite (solid Fe(III) oxide) will be used as well to study the transformation of Fe(III) to the bioreduced form, Fe(II), with the target of producing biovivianite after the period of microbial reduction. The sorption of P onto Ferrihydrite and its subsequent conversion to biovivianite will be investigated as well.

Within this task, ESR8 will test different products obtained from microbial transformation of P containing Fe(III) oxides in order to test their efficiency as P and Fe sources. This will depend on obtaining these products in the near future. However, cucumber seeds were already raised in a nursery on 28th January 2020 and transplanted on 18th February 2020. These seedlings will be used for further experiments.

Task 4: Amelioration of soils by addition of vivianite or other solids containing Fe and P (US, KUL, UNIVIE)

> *The effect of addition solids containing Fe and P on soil fertility and quality will be investigated, prerequisites for achieving soil amelioration will be outlined, guidelines and protocols for agricultural applications will be developed.*

ESR10 synthesized vivianite that may be used as standard material to investigate its effect on soil fertility and to compare it to other P and Fe containing phases produced in P-TRAP. Additional laboratory studies on the dynamics of solid-bound Fe and P were performed by ESR10 (vivianite dissolution and transformation) and ESR9 (P interactions with schwertmannite), as detailed in the description of Task 3 of WP3.

Clearly, the development of guidelines and protocols for agricultural application that are central to Task 4 will depend on outcomes of field and laboratory experiments leading towards deliverable D1.5 that is due in August 2022. Results of field experiments are not yet available at this time. However, the selection of sites, soils and materials that has been undertaken in milestones accomplished in February 2020 are important steps towards the stated goals of this task.

1.1.2 Work Package 2 – Novel method for long-term P binding in lake sediments

WP 2 is led by UBT. 4 beneficiaries are contributing to WP 2: UU (ESR 6 and 11), UBT (ESR 9), EAWAG (ESR 7) and GEOS (ESR 4). All ESRs have been started.

WP 2 has no dedicated work package management on top of the general project management.

1.1.2.1 Executive summary WP 2

The overarching goal of WP 2 is to apply Fe-containing by-products binding P in lake waters. To test these products, experimental lakes have been selected (milestone MS3). The selected lakes are three unstratified lakes in the Netherlands that have been treated with iron in the past and a seasonally stratified lake in Germany. All lakes are in recreational use and are regularly affected by blue algae blooms due to eutrophication. ESR6 started to investigate the release of P, which is initially bound to iron oxide when the latter are exposed to dissolved sulfide. This process is key for the mobilization of solid-bound P in lake sediments. ESR11 has started to investigate the binding form of solid-bound Fe and P in sediments from lakes in the Netherlands, which have been treated with iron salts in the past. ESR9 started analysing the sediment biogeochemistry of the stratified lake *Kleiner Brombachsee*. He further performed first test experiments on the adsorption of P on the P-sorbent schwertmannite. ESR7 performed first experiments on the formation of Fe(III)-precipitates by Fe(II) oxidation in the presence of organic compounds and on the transformation and P retention of Fe(III)-precipitates over time that are also relevant for the mechanistic understanding of P dynamics in lakes.

1.1.2.2 Progress summary per WP partner

UU: First sequential extractions of Fe and P on sediment cores have been performed, in collaboration with UBT. These sequential extractions are used to characterize the binding form (adsorbed or structurally bound) and the corresponding phase (e.g. phosphate mineral, adsorbed onto iron oxide) of Fe and P in the sediments. In the next future these techniques will be applied to material from a sediment core, which has been taken from a lake in the Netherlands (Sloenen). UU started preparing a field campaign in March for retrieving fresh cores from the Reeuwijk Lake Complex in the Netherlands. Next to this, UU started to determine the release of P upon the reaction of Fe oxides. The experimental set-up has been developed and first tests have been performed. Additionally, methods for characterizing Fe containing solids are currently being tested. This includes FT-IR, Raman spectroscopy, XRD, and electron microscopy.

UBT: The work so far has been focussed on getting the ESR acquainted with experimental techniques essential in 1) structural characterisation of iron minerals, 2) determination of phosphate adsorption kinetics and equilibria, 3) initiated exchange of solid-phase characterisation methods in collaboration with the UU, and 4) exploratory characterisation of a lake reservoir. Aim is to assess the fate of iron in lake sediments as well as analyse the potential of supplied iron minerals in combatting internal phosphorus loading. To gain experience with the main lab techniques as mentioned in 1 and 2, the PO_4 adsorption on schwertmannite was investigated as well as on iron coated sands as supplied by *Aqua Minerals* (Non-academic partner organisation). Results will be used in sediment incubation experiments. With respect to the characterisation of a lake reservoir, UBT initiated contacts with the *Wasserwirtschaftamt Ansbach* who governs a few artificial reservoirs / lakes in the Nürnberg area. Four sediment cores were extracted and analysed from the lake *Kleiner Brombachsee* in Bavaria, Germany.

EAWAG: A first experiment on the aging of fresh Fe(III)-precipitates over 10 days was performed and the solids were analysed with synchrotron-based X-ray absorption spectroscopy and other methods to get acquainted with experimental procedures and analytical techniques. In the experiment, the aging of precipitates formed in the absence and presence of Ca and silicate and consequences for P retention were studied. The experiments confirmed and expanded insights from previous work, and pointed to the importance of CO_2 outgassing as controlling factor in aging experiments. A second test experiment on the effects of different organic compounds on the formation of fresh Fe(III)-precipitates was initiated by the end of the first-year reporting period. First steps were also taken to study the structure and composition of water treatment residues from AquaMinerals that are going to be used in P-TRAP systems.

GEOS: A first focus laid on the study of raw material properties, which includes schwertmannite properties during batch experiments. All studies yet were carried out with the model solution of phosphorus. Until now the data about the moisture content, adsorption capacity and kinetical parameters of raw schwertmannite were obtained. The collaboration with UBT has been initiated to schedule the first secondment at UBT, planned for 2021. This will help to gain better understanding of schwertmannite-based adsorbents in terms of P-removal from waters, particularly in lakes.

1.1.2.3 WP 2 - Task Report

Task 1: Determine the coupling of Fe and P dynamics in selected lakes (UU, UBT, EAWAG)

> *In selected lakes, seasonal dynamics of Fe and P will be investigated in the water column and sediments including ecological characterization and rigorous characterization of Fe and P speciation*

In 2018, an exploratory investigation has been performed in collaboration with DELTARES. Surface water samples and sediment cores have been collected from seven lakes in the Netherlands, of which four have been treated with Fe in the past (Table 1). This investigation forms the basis for the selection of suitable lakes in the Netherlands and results will be used within P-TRAP.

Table 1: Description of lakes investigated in the preliminary study. Taken from Fauqué (2018)

Region	**Reeuwijk**						**Loosdrecht**				**Friesland**			
Lake	**Gravenbroek**		**Sloene**		**Groot Vogelenzang**		**Vuntus**		**Terra Nova**		**Botmeer**		**Nannewijd**	
Core position in lake	Shore-ward	Middle	Shore-ward	Middle	Shore-ward	Middle	Shore-ward	Middle	Shore-ward	Middle	Shore-ward	Middle	Shore-ward	Middle
Core identifier	**GK-P**	**GK-M**	**SL-P**	**SL-M**	**GV-P**	**GV-M**	**VT-P**	**VT-M**	**TN-P**	**TN-M**	**BM-P**	**BM-M**	**NW-P**	**NW-M**
Sampling coordinates	52.0382141, 4.7230837	52.0380607, 4.7343453	52.0522319, 4.7407230	52.0523697, 4.7422917	52.0328666, 4.7498438	52.0340743, 4.7524523	52.2087451, 5.0707376	52.2121471, 5.0745517	52.2188980, 5.0442334	52.2222686, 5.0402821	53.0725875, 5.8737454	53.0750803, 5.8725495	52.9425324, 5.8634189	52.9475280, 5.8673798
Surface area (ha)	105.22		9.21		18		88		85		33		86.99 (treated area)	
Average depth (m)	2.1		2.3		1.75		1.4		1.4		0.5		0.8	
Treatment	-	-	FeCl$_3$		FeCl$_3$		-	-	FeCl$_3$		-	-	FeCl$_3$	
Treatment quantity (g m^{-2})	-	-	**178**		**100**		-	-	**33**		-	-	**53.5 (on 12.01 ha)**	**10.7 (on 56.61 ha)**
Treatment Location	-	-	Surface waters		Top 0 to 15 - 20 cm of sediments		-	-	Surface waters		-	-	Water colum	
Treatment method	-	-	Wind driven microcurrent		Boat application to sediment		-	-	Wind driven microcurrent		-	-	Boat application to	
Treatment quantity verification	-	-	No		High accuracy location based positioning		-	-	No, wind driven microcurrent dispersal		?	?	High accuracy location based positioning	
Heterogenity of Fe treatment between cores	0		+		+ +		0		+ +		* * *		+ + + +	+
Average total lake treatment Fe recovery (%)	**-**	**-**	**87**		**244**		**-**	**-**	**99**	**99**	**?**	**?**	**530**	**530**
Start of treatment	-	-	Apr-2014		1989		-	-	2010		-	-	Oct-1994	
Treatment duration	**-**	**-**	**~ 3 years**		**~4 weeks**		**-**	**-**	**~1.5 years**		**-**	**-**	**5 months**	
Literature Background Fe (mmol/kg)	-	-	716 (top 0 to 5-10 cm)	603 (top 0 to 5-10 cm)	430 (top 0-5 cm)		-	-	394 (top 0-2 cm)		-	-	-	-
Water residence time	-	-	> 2 years		35 days		1.5 years		1 year		37 days		>2 years	
Literature reference	Brouwer Group, 1993; Torenbeek, 2013		B-Ware, 2018; Frank, Tableau Public, 2019[1]		Quaak et al., 1993		Boers, 1991; Van Liere et al., 1987		Ter Heerdt et al., 2012; Mettrop, 2009		Witteveen & Bos, 2012		Veeningen, 1996; Waterschap Friesland, 1995	

From each lake two sediment cores have been taken, pore waters have been collected, sediments were sliced and the solid phase has been analysed. Exemplarily, pore water profiles from the three lakes from the *Reeuwijk Lake Complex* (Fig. 4) are shown in Fig. 5. The pore profiles obtained for the lake *Sloenen* suggest that addition of Fe has been affecting the P dynamics in the sediment. Pore water concentrations of Fe and P are closely correlated, indicating that release and removal of P to or from the pore water is controlled by the redox cycling of Fe in the sediment. That is, when Fe oxides, which are containing P, are reductively dissolving in the deeper parts of the sediment, Fe^{2+} and P are released into the pore water. The concentration gradients in the pore water indicate that both constituents are diffusing upwards and the decrease in the concentrations of Fe^{2+} and P can be ascribed to the oxidation of Fe^{2+} in the upper part of the sediment where oxygen is available. The pore water concentrations in the lake *Sloenen* are higher compared to the other two lakes, which suggests that efficient P and Fe cycling in the sediment has led to an accumulation of reactive P in the sediment. The pore water concentrations

Fig. 4: Location of the *Reeuwijk Lake Complex* and a map of the various lakes.

in the lake *Groot Vogelenzang* are higher compared to the reference lake '*s Gravenhagen*. However, the concentrations of dissolved Fe were below detection limit and no indications for active Fe redox cycling were obtained.

The next sampling campaign as a collaboration between UU and UBT is planned for March 2020 in order to collect sediment cores for analysing the binding form of Fe and P in the sediments. Several methods are planned to be used and in preparation, such as

- photospectrometry to determine iron, phosphorus, ammonium and sulfate in porewater
- micro-sensor profiling to determine pore concentrations of oxygen, pH and sulphide
- sequential extraction to analyse the solid-phase of the sediment
- mineral characterisation by X-ray diffraction (XRD), Fourier-Transform-Infraredspectroscopy (FTIR) and surface area measurement by Brunauer-Emmett-Teller (BET)
- creating sediment-incubation set-up in which anoxic conditions

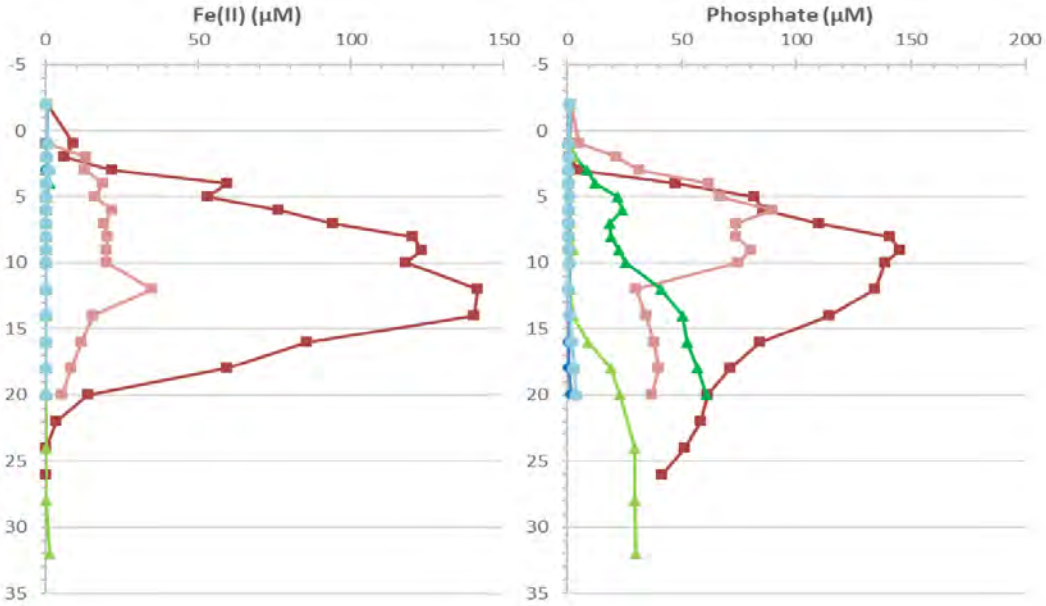

Fig. 5: Pore water profiles of Fe(II) and P obtained from lakes from the *Reeuwijk Lake Complex*, the Netherlands (taken from Fauque, 2018). Two of the lakes have been treated with Fe in the past: *Sloenen* (squares) and *Groot Vogelenzang* (triangles). The third lake, *'s Gravenbroek* (circles) has not received Fe amendment in the past

These analyses will provide information on the differences in Fe and P cycling in the lakes, to which iron containing solution has been added in the past. Next to the above-mentioned lakes in the Netherlands, the partially eutrophic *Brombachsee* reservoir is an optional field site.

This artificial reservoir contains a highly eutrophic small settling lake (*Kleiner Brombachsee*, area of 2 km^2, Fig.6) which is separated by a dam from a deeper main lake (*Grosser Brombachsee*). This lake suffers less from harmful algae blooms. In the *Kleiner Brombachsee* 2 exploratory cores have been taken. The cores were sliced and porewater concentrations of sulfur, iron and phosphate were investigated (Fig. 7).

The cores were both considerably reduced, with oxygen penetration depths of just 7 mm. As SO$_4$ reduction rates and oxygen penetration depth are correlated sulfide levels were high in both locations. Peaks of sulfide up to 150 µM were observed. In location 1 sulfide levels were lower than for location 2. As iron and sulfide precipitate as metastable FeS, iron concentrations are consequentially higher in location 1. The precipitation of FeS can also be observed in the porewater profiles of the sulfide and iron.

Fig. 6: Bathymetric map of *Kleiner Brombachsee* and locations with GPS data of exploratory cores taken.

Free phosphate concentrations are considerable in the porewaters of both cores. Ranging from 50-150 µM in location 1 and from 0-100 µM in location 2. Clearly there is a phosphate efflux from the sediments into the overlying water. Solid-phase samples were stored in oxygen-free atmosphere and will be analysed together with ESR11 in Utrecht. This to ensure that our methods of solid-phase characterization will be similar and comparable.

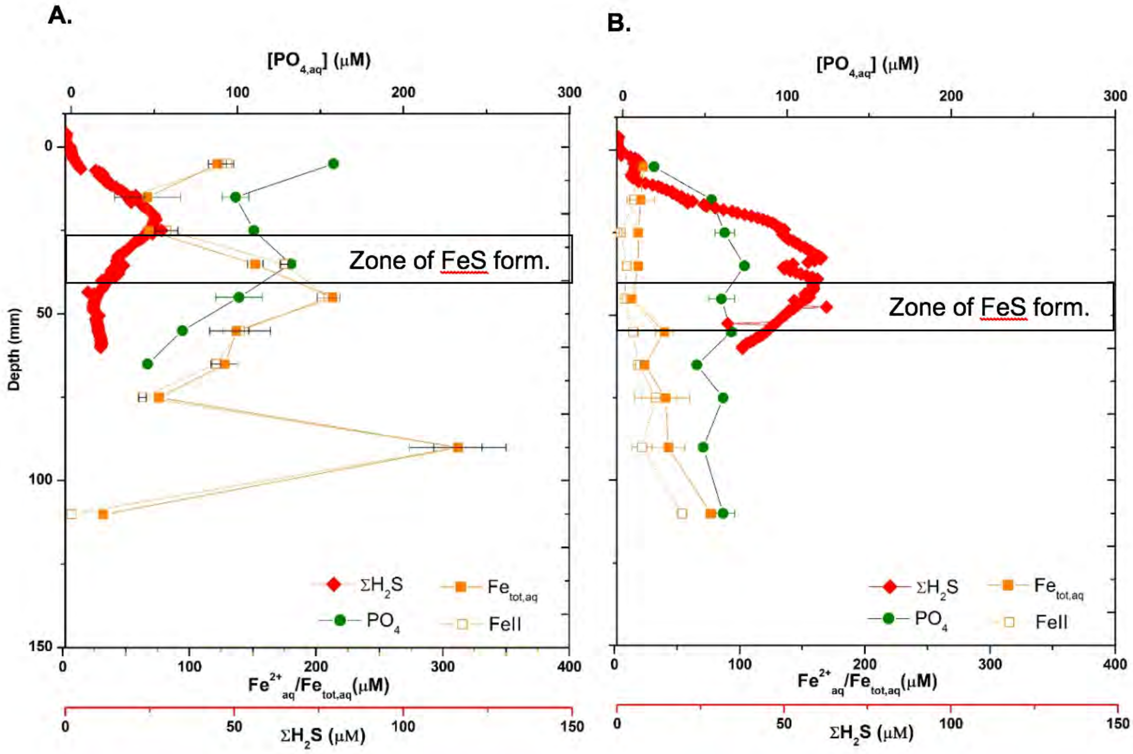

Fig. 7: Pore water concentrations of ortho-phosphate PO$_4$ (●), total iron Fe$_{tot}$ (■), Ferrous iron Fe^{2+} (□) and total sulfide $\sum H_2S$ (◊) for A) location 1 and B) location 2.

In the next step, a sequential procedure will be applied to the cores following a protocol adopted from UU. This will be part of the secondment of ESR1 at UU. ESR7 will work on the formation and transformation of Fe(III)-precipitates under oxic conditions, which will offer mechanistic insights into processes that are also relevant for coupled Fe-P dynamics in lakes, and are thus expected to contribute to a better process-based system understanding.

The deliverable D2.1, due in project month 24, is on track.

Task 2: Testing efficiency of adding by-products of water treatment to bind dissolved P in lakes (UU, UBT, GEOS)

Binding of P to by-products of water treatment will be determined.

First tests have been executed to initially characterise adsorption capacities, which will be later used in subsequent experiments and modelling. Results will be reported in deliverable D2.3.

The adsorption isotherm of iron coated sand, provided by AquaMinerals, was determined by batch adsorption experiments with differing initial concentrations of phosphate. Data was subsequently fitted using two different models, being Langmuir and Freundlich (Fig. 8).

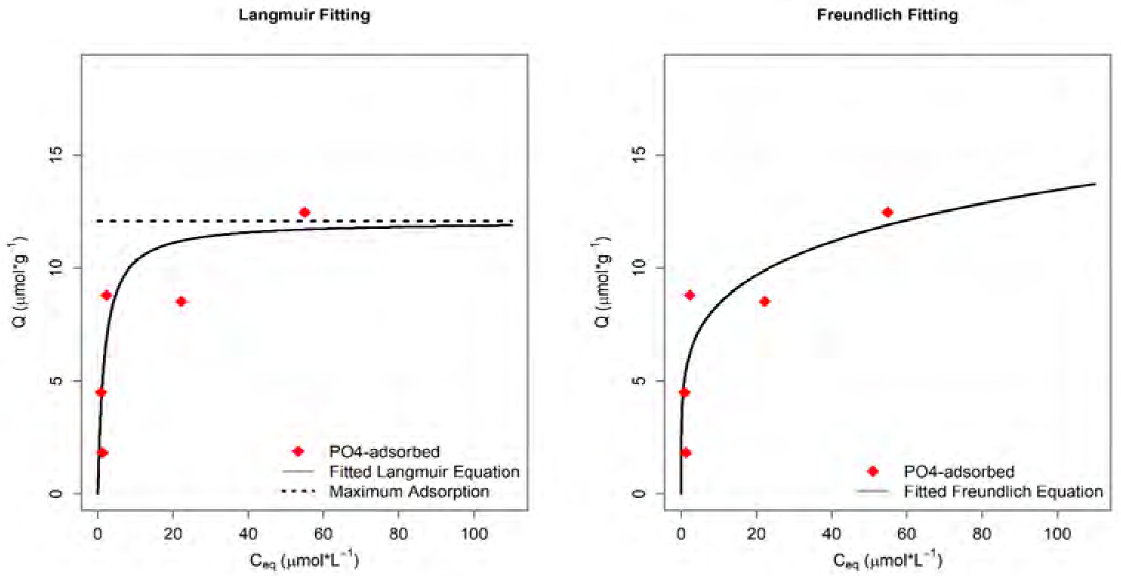

Fig. 8: Fitting of the adsorption isotherm of Iron coated sand using A) the Langmuir model for adsorption and B) the Freundlich equation.

The maximum adsorption of the iron coated sand was determined to be 12 µmol*g^{-1} from the Langmuir model of adsorption. These iron coated sands will later be used in the sediment incubation experiments to observe effects on P-release from the sediment.

To get acquainted with spectrophotometric techniques as well as FTIR, first experiments were performed to characterize phosphate adsorption onto schwertmannite under different pH. Schwertmannite is a mineral formed under acidic sulfate-rich conditions, mainly acidic mine drainage sediment. The iron-sulfate hydroxide is metastable and releases more sulfate as pH is increased. This results in behaviour counter-intuitive to that of stable iron oxides containing no sulfate. Namely that anion-adsorption is greatest at low pH. A kinetic experiment was performed to observe this effect. Furthermore, studies with a model solution of P were performed to obtain data about the moisture content, adsorption capacity and kinetical parameters of raw schwertmannite.

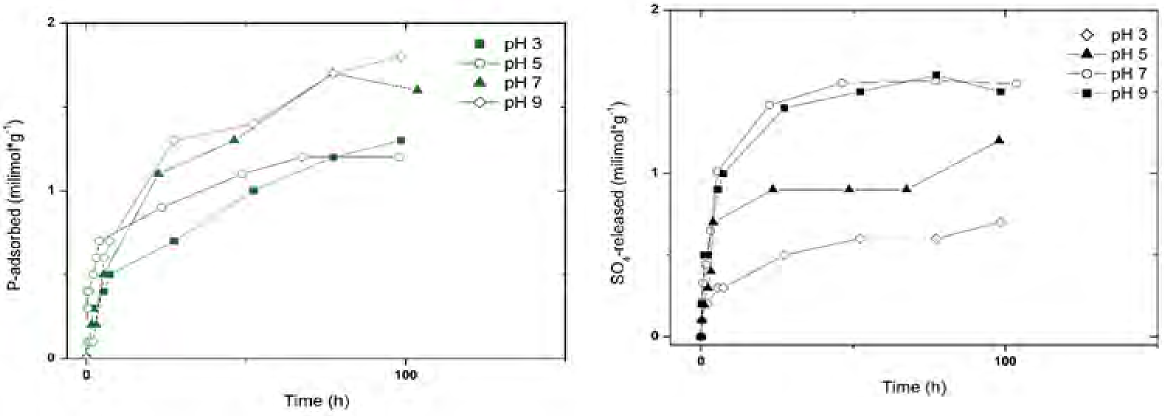

Fig. 9: a) PO_4 - adsorption on Schwertmannite under differing pH conditions, b) the associated SO_4 - release

As can be observed from Fig. 9 higher pH has more favourable phosphate adsorption kinetics. Interestingly, the same pattern is observed for sulfate release. From Wang et al. 2015 it has been observed that pH causes a difference in complexation of the sulfate in schwertmannite. At high pH, sulfate is more weakly bound as an outer-sphere complex, whereas at lower pH it is more strongly bound in the structure as an inner-sphere complex. This means that ligand exchange will be easier at higher pH as is clearly observable in our data. So, during our kinetic experiment we arrive at different kinetic areas depending on which pH we have.

Tests on the efficiency of adding Fe-containing by-products to Dutch lakes are planned in the future and in collaboration with Waternet as one of the partner organisations. A meeting to discuss this in detail has been scheduled for March.

Task 3: Design procedure for Fe supplementation of the lakes (UU, UBT)

> *The speciation of Fe and P will be determined in all investigated systems (soils, sediments, drainage, bioreactors) and their changes due to phase transformations will be elucidated.*

This task depends on data to be generated in laboratory experiments and has not been addressed so far. The deliverable D2.3 related to this task is due in the month 24.

Task 4: Determine potential of Fe addition to lakes for achieving P immobilisation in sediments (UU, UBT, EAWAG)

> *Effects on nutrient dynamics and ecology upon addition of Fe will be investigated in test sites and in lakes to which Fe has been added in the past.*

This task depends on data to be generated in laboratory and field experiments. The survey on long-term effects of Fe addition has been started and will last through years 2020 and 2021. Deliverable D2.4 and D2.5 related to this task are due in month 40.

1.1.3 WP 3 – Mechanistic studies on P dynamics during Fe phase transformation

WP 3 is led by EAWAG and includes all 9 beneficiaries. Regarding the management of WP3, management will involve personal exchange and conference calls as required to coordinate efforts by the different ESRs. Twice a year, thematic exchange with respect to WP3 among all involved partners will be ensured by meetings during the annual meetings and training events or during separate conference calls.

1.1.3.1 Executive summary WP 3

In the context of P-trapping systems examined within P-TRAP, WP3 focus on mechanistic studies on the formation and transformation of Fe solids under varying chemical conditions and their consequences for P binding and solubility. Mechanistic aspects are considered in all ESR projects to a certain degree. The projects of ESR3 (UNIVIE), ESR6 (UU) and ESR7 (EAWAG) have a clear focus on laboratory-based mechanistic studies that involve the use of advanced experimental and analytical approaches.

ESR6 learnt to use a flow-through reactor system to study Fe-oxide transformation by sulfidation under anoxic conditions, ESR7 performed a first test experiments on Fe(III)-precipitate aging under oxic conditions and on the effects of organic compounds on the formation of Fe oxidation products to familiarize with experimental and analytical techniques, and ESR10 performed first test experiments on the oxidative transformation of vivianite. ESR2 compiled a common set of extraction procedures for the characterization of solid-phase P and Fe to be used within P-TRAP (milestone 5), in collaboration with other ESRs.

1.1.3.2 Progress summary per WP partner

UU: Work performed so far belongs to both, WP 2 and WP 3 (see details in chapter 1.1.2.2 and 1.1.2.3).
UNIVIE: Different batches of vivianite were synthesized with varying synthesis parameters. Attempts were made to produce minimally oxidized vivianite by modifying standard protocols, and also to obtain different particle sizes and, hence, surface areas to compare the reactivity. The synthesized vivianite has been characterized regarding its mineralogy (X-ray diffraction, Raman), surface area (BET), particle size, and Fe(II)/Fe(total) ratio (photometry). A time slot has been secured at the SEM facility in the coming weeks for the microscopic characterization of the vivianite.

UBT: Work performed so far belongs to both, WP 2 and WP 3 (see details in chapter 1.1.2.2 and 1.1.2.3).

EAWAG: Work performed so far belongs to both, WP 2 and WP 3 (see details in chapter 1.1.2.2 and 1.1.2.3).

UNIMAN: No scientific work related to WP3 has been performed in the first project year due to delays associated with visa problems. Current activities focus on preparing chemical and biological safety assessments. Laboratory experiments will be started towards the end of February 2020 by growing *Geobacter sulfurreducens* and using cells of this Fe(III)-reducing bacterium to reduce synthetic Fe(III) oxides (ferrihydrite) and soluble Fe(III), in the presence and absence of phosphate, with the aim of synthesizing reference “biovivianite” materials. Subsequent experiments will be performed with sediments, soils, and waste materials in bioreactor systems. The obtained solids will be characterized with a broad range of techniques, including synchrotron X-ray based spectroscopies.

US: Until February 2020, no work directly related to WP3 has been performed. Different vivianites have been synthesized for studying their solubility and potential release of P and Fe (in collaboration with ESR2). In February 2020, we start experiments with synthetic vivianites that differ in elemental composition (P content, Zn and Mg incorporation) to assess their solubility and effect on P uptake by plants in artificial growing media, as a first approach to investigating the P fertilizer effect of vivianite from different origins.

KULeuven: No work related to deliverables D3.1 and D3.2 associated with WP3 has been performed within the first project year. A large effort was put into the compilation of extraction procedures for the characterization of solid-phase P and Fe in soils and sediments to be used within P-TRAP (milestone MS5). Protocols for the extraction of P and Fe from soils were mainly contributed by KUL and US, respectively. UU contributed the standard procedures for the extraction and analysis of different fractions of P and Fe from sediments.

GEOS: No work related to WP3 has been performed within first year.

DELTARES: No work related to WP3 has been performed within first year.

1.1.3.3 WP 3 - Task Report

Task 1: Systematically investigate transformations of P-containing Fe(III) oxides in laboratory experiments (EAWAG, UU)

> *Mechanisms and kinetics of the transformation of P-containing Fe minerals upon aging or change in redox conditions will be studied and the controlling factors will be determined.*

Aging of fresh Fe(III)-precipitates under oxic conditions and effects on P retention

ESR7 performed a first aging experiment with fresh Fe oxidation products to gain experience with the experimental setup for Fe(III)-precipitate formation and transformation experiments and analytical techniques. In the experiment, fresh Fe(III)-precipitates were synthesized by the oxidation of 0.5 mM Fe(II) in 8 mM Na-bicarbonate or 4 mM Ca-bicarbonate background electrolyte adjusted to pH 7.0 with CO_2, without or with Si (0.5 mM) (Na, Ca, Na+Si, Ca+Si electrolytes) and with 0.125 mM P (0.25 P/Fe). Oxidation and Fe(III)-precipitate formation was completed within 4 h and was followed by precipitate aging in the synthesis solution for up to 10 d. After given reaction times (4 h, 1 d, 3 d, 6 d, 10 d), filtered solutions were collected for the analysis of dissolved element concentrations by ICP-MS and solids for recovered from filter membranes for characterization by Fe K-edge EXAFS spectroscopy.

Dissolved P concentrations after 4 h revealed that the extent of P uptake by the fresh Fe(III)-precipitates increased in the order Na < Ca < Na+Si < Ca+Si (Fig. 10). Along the same sequence, the re-solubilisation of P during aging was reduced. Thus both Ca and Si positively affect P removal by fresh Fe(III)-precipitates as well as P retention during precipitate aging, due to various coupled mechanisms. For the Na electrolyte, where lowest initial P removal and highest re-solubilisation was observed, Fe K-edge EXAFS spectra pointed to the partial transformation of ferrihydrite with high P sorption capacity to poorly crystalline lepidocrocite with lower P sorption capacity as probable cause for P release during aging (Fig. 11). The first results, in combination with data from earlier work, suggested that the extent of CO_2 outgassing and resulting pH increase during aging may strongly affect the extent of precipitate transformation and P retention, and thus needs to be constrained and monitored in future aging experiments.

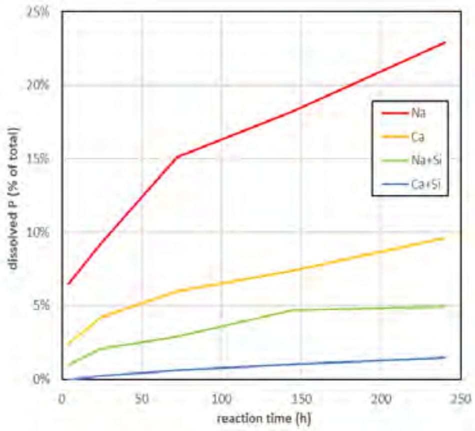

Fig. 10: Fractions of dissolved P as % of total initial P in the precipitate suspensions in Na, Ca, and Na+Si, Ca+Si background electrolytes. The first data after 4 h represent dissolved P concentrations after Fe(III)-precipitate formation, the increase over time is associated with precipitate aging.

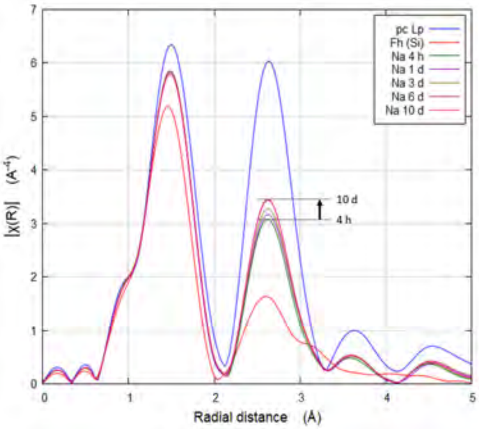

Fig. 11: Fourier-transformed Fe K-edge EXAFS spectra of Fe(III)-precipitates in Na electrolyte in comparison with reference spectra. The fresh precipitate was a mixture of poorly crystalline lepidocrocite (pc Lp) and ferrihydrite (Fh (Si)). Aging led to an increase in the peak at ~2.7 Å that points to ongoing ferrihydrite transformation into lepidocrocite.

A second test experiment was recently started on the effects of organic compounds on the structure, P uptake and colloidal properties of fresh Fe(III)-precipitates, with the aim to optimize the experimental setup. As organic compounds, citric acid, galacturonic acid, polygalacturonic acid and Leonardite humic acid were considered, which vary in terms of organic functional groups, molecular weight and structural complexity. The evaluation of this experiment is still ongoing.

Sulfidation of Fe(III)-(oxy)(hydr)oxides and consequences for P retention

ESR6 aims at determining the mechanisms and kinetics of phosphate release during the sulfidation of Fe(III)-(oxy)(hydr)oxides (Fe-oxides). The reaction of sulfide with Fe-oxides is considered a relevant pathway for the mobilization of solid-bound Fe and P in sediments. To investigate the kinetics of Fe oxide sulfidation, we use mixed flow-through reactors, which allow measuring reaction rates at controlled steady-state conditions.

The experimental system, which has been set up, consists of multiple flow-through reactors (Fig. 12). The system has been tested for leakage, flow rates were calibrated, and test runs were performed with inert electrolytes. Protocols have been developed for preparing anoxic, sulfide containing solutions, and for designing a sampling scheme. The analytical procedures for measuring dissolved iron, phosphate and sulfide in the outflow of the reactors have been tested. Furthermore, a procedure has been tested to recover the solids at the end of the experiment under anoxic conditions for detailed characterization. The method is based on pumping N_2 gas through the flipped over reactor. The idea is to collect the solids on the membrane filter (Fig. 13). The Fe-oxide lepidocrocite (γ-FeOOH) has been chosen for our first experiments. Suspensions containing lepidocrocite with and without adsorbed phosphate have been prepared.

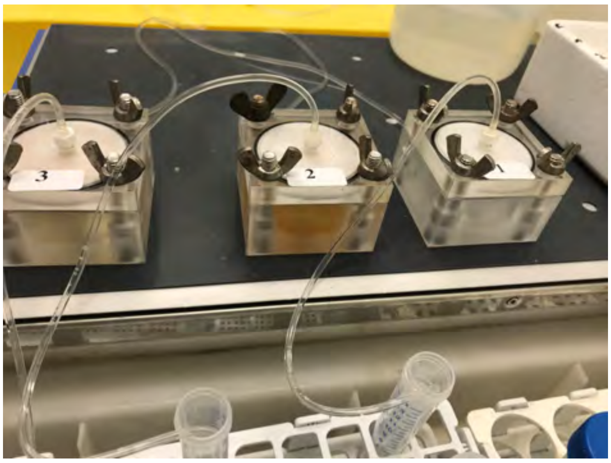

Fig. 12: Flow-through reactor setup. The picture shows the flow-through reactors which are installed on a stirrer plate to keep the suspension well mixed throughout the experiment. Solutions are pumped through the reactor at controlled flow rates using a peristaltic pump. The reactor contains a magnetic stir bar. The solids are retained in the reactors by membrane filters which are installed before the outlet opening at the top.

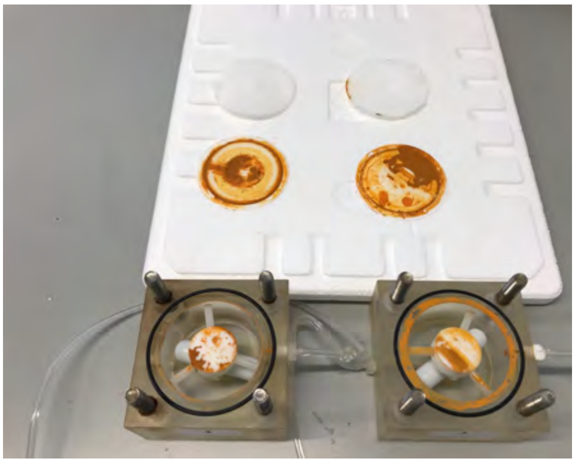

Fig. 13: Testing the recovery of reacted solids at the end of the experiment. The majority of the solids could be recovered from the membrane filters, but a part was sticking behind the holder of the magnetic stir bar. For this reason, another type of magnetic stir bar was tested which does not need a holder.

For testing the experimental design, the reactors were filled with deionized water and the breakthrough curve of a 0.1 M NaCl solution has been measured by monitoring the electric conductivity in the outflow (Fig. 14). The shape of the break-through curve can be compared to the theoretical curve based on the flow rate, the volume of the reactor, and the assumption that the reactor is well-mixed. The test demonstrated that the reactors behave as well-mixed reactors.

First experiments with lepidocrocite and sulfide have been performed at pH 8.3. The pH has been selected based on preliminary experiments and will be varied systematically in subsequent experiments. The pH is maintained by a buffer added to the sulfide solution. pH measurements in the outflow indicate that pH changed by less than 0.3 units. Throughout the experiments, aliquots of the outflow were collected for determining the concentrations of phosphate, iron and sulfide. Results show that the concentrations of sulfide in the outflow increased at the beginning of the experiment and then reached a steady state (Fig. 15).

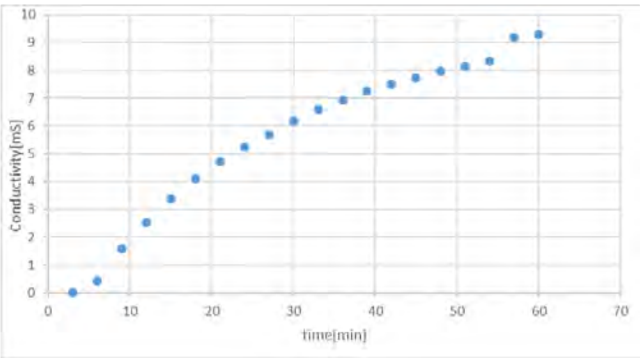

Fig. 14: Breakthrough curve of 0.1 M NaCl though the flow-through reactor.

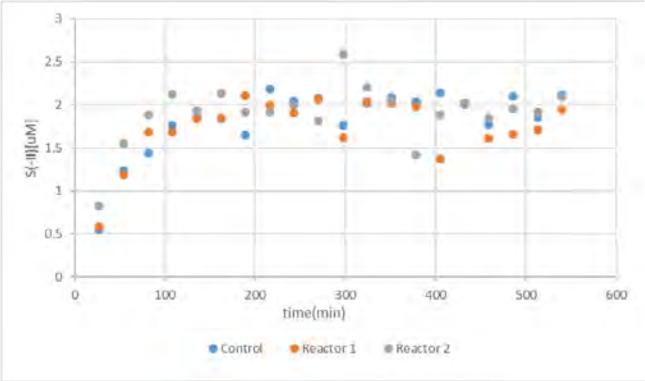

Fig. 15: Time evolution of sulfide concentrations in the outflow of the reactors during the lepidocrocite sulfidation experiment. The control reactor does not contain Fe oxide.

However, relatively large variations (>10%) in the effluent sulfide concentrations were observed over time, which currently impede the precise determination of sulfide consumption rates. We are therefore working on improving the robustness of the sulfide determination. Also, other measures are currently being tested to improve the quality and significance of the results, such as adjusting the flow rates. In first experiments with Fe-oxides with adsorbed phosphate, a pulse of increased phosphate concentration was observed when sulfide started to enter the reactors (Fig. 16).

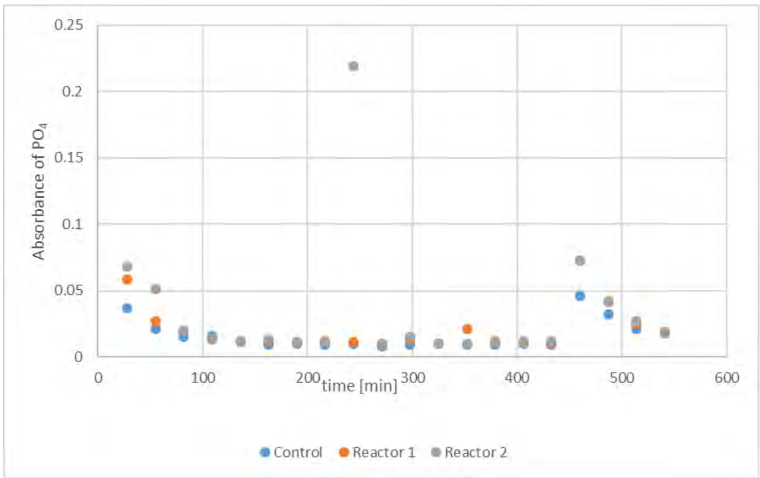

Figure 16: Time evolution of effluent phosphate concentrations in sulfidation experiments with phosphate-sorbed lepidocrocite. The concentration of P was measured by a photometric method and the absorbance is plotted. The increase in absorbance after about 450 min is due an interruption of the flow for about 8 hours. The control reactor does not contain Fe-oxide.

However, not all adsorbed phosphate became released. That is, phosphate release continued at a constant pace after the initial pulse. Resuming the pumping after an interruption of several hours resulted in a significant increase in phosphate concentrations in the outflow. This supports the conclusion that the release of phosphate due to Fe-oxide sulfidation is controlled by reaction kinetics and occurs on the time scale of hours to days.

Outlook

In continuation of the described work, ESR7 will perform further experiments on precipitate aging using an improved experimental setup with better control of CO_2 outgassing and pH increase, and for a larger set of environmentally relevant Fe(III)-precipitates. In parallel, further experiments on the role of organic compounds will be performed, using improved experimental protocols designed on the basis of the first test experiment. ESR6 will further optimize the experimental design, and perform flow-through reactor experiments in which the suspension pH, type of Fe-oxide and the binding form of phosphate (adsorbed versus co-precipitated) will be systematically varied. In a later step, ESR6 plans experiments on the conversion of iron sulfides into iron phosphates and vice versa.

Task 2: Develop kinetic models for transformations of P containing Fe phases (all BFs)

> *Empirical rate laws for the transformation of Fe phases obtained from laboratory experiments will be integrated and tested in models for the Fe and P dynamics in the soils, sediments, drainage systems and bioreactors.*

This task depends on data to be generated in laboratory experiments under task 1 and on results from field experiments and has not been addressed so far. Deliverables related to this task are due in the months 36 and 40.

Task 3: Investigate the temporal dynamics of solid-bound Fe and P in the studied systems (all BFs)

> *The speciation of Fe and P will be determined in all investigated systems (soils, sediments, drainage, bioreactors) and their changes due to phase transformations will be elucidated.*

First laboratory experiments on the transformation of Fe(III)-solids and consequences for P retention have been initiated by ESR6 and ESR7, as described above related to Task 1 (experiments on the aging of Fe(III)-precipitates under oxic conditions, on the impact of organic compounds on precipitate formation, and on Fe(III)-(oxy)(hydr)oxide transformation by sulfidation under anoxic conditions).

Additional laboratory studies on the dynamics of solid-bound Fe and P were performed by ESR10 (vivianite dissolution and transformation) and ESR9 (P interactions with schwertmannite), as detailed in the following sections.

Dissolution of vivianite under anoxic and oxic conditions

ESR10 synthesized different batches of vivianite with varying synthesis parameters. Attempts were made to produce minimally oxidized vivianite by modifying standard protocols, and to obtain different particle sizes and, hence, surface areas to compare the reactivity. The synthesized vivianites have been characterized for their mineralogy (X-ray diffraction, Raman), surface area (BET), particle size, and Fe(II)/Fe(total) ratio (photometry). A time slot has been secured at the SEM facility in the coming weeks for the microscopic characterization of the vivianites.

Dried synthetic vivianite in pristine (no contact with air) and oxidized form (after contact with air) was analysed using a Raman spectrometer (Horiba Jobin Yvon LabRAM-HR Evolution spectrometer) using a 473/532/633 nm laser. Due to the very high radiation-sensitivity of vivianite, extreme care was required to avoid artefacts. The blue laser line was used with low intensity, resulting in longer runs. After each run, the sample was checked for colour changes that are indicative of radiation damage. If the samples were analysed under oxic conditions, only broadened peaks with a slight shift to higher wavenumbers could be obtained, indicating a disturbed or amorphous structure. Therefore, a small anoxic chamber was designed and fabricated in house that allowed Raman measurements in an inert (N_2) environment without the interference of O_2. This setup also allowed using a higher laser power without inducing radiation artefacts. The characteristic sharp peak at 950 cm^{-1} due to PO stretching, the pattern between 100 to 600 cm^{-1} arising from OPO bending as well as the broad peak between 2700 to 3700 cm^{-1} that results from OH stretching were observed. Efforts are currently underway to develop the analytical protocol to analyse (partially) oxidized vivianite and to interpret the data.

Synthetic vivianite with 30% Fe(III) was incubated under oxic and anoxic conditions at environmentally relevant pH (4-8) for 41 days. Briefly, 1.99 mM vivianite were suspended in 0.01 M NaCl electrolyte. The pH was buffered with 0.005 M of either PIPPS (pH 4 and pH 8), NaOAc (pH 5), MES (pH 6), or MOPS (pH 7) and adjusted with 0.5 M NaOH or HCl. All batches were prepared anoxically. Suspension vials were protected from light to prevent photochemical reactions. The dissolution and oxidation of vivianite were both highly pH dependent. In dissolution experiments under anoxic conditions, the Fe oxidation state of the vivianite remained constant at the initial level of ~30% Fe(III), confirming the absence of oxygen. In the dissolution experiments under oxic conditions, the solid-phase Fe(III) fraction increased over time and with pH, and reached 100% in the oxic incubation at pH 8 after 41 days. The overall mobilization of phosphate and Fe was much higher in anoxic incubations than in oxic incubations, except at pH 4. Vivianite dissolution rate and solubility increased with decreasing pH. Thus, the highest dissolved concentrations of phosphate (207 µM) and Fe(tot) (1000 µM) were measured in anoxic samples at pH 4. A high initial dissolution was observed, which levelled off over time or even decreased for oxic samples at lower pH, resulting in a negative dissolution rate. For the oxic incubations at low pH, rapid initial dissolution of vivianite may have been followed by the formation of amorphous Fe(III)-phases that probably sorbed the previously released phosphate. Sorbed phosphate might interfere and hinder the formation of new crystalline Fe(III)-phases, similar to the reported effects of phosphate on Fe(III)-precipitate formation by Fe(II) oxidation and on Fe(III)-precipitate crystallization. These interpretations are in line with XRD results, which showed that the only crystalline phase in the incubations was vivianite, and that no other crystalline phase formed over time. Microscopic observations are expected to provide further insights into these phase transformation processes.

With respect to vivianite in P-TRAP systems, first experiments have also been initiated on the synthesis of biovivianite (ESR5) and the synthesis and use of vivianite (ESR8), as briefly described in Task 3 of WP1.

Adsorption of phosphate onto schwertmannite

ESR9 performed first experiments on the adsorption of phosphate onto schwertmannite and familiarized with analytical techniques for the characterization of Fe-phosphate interactions and Fe solids. Phosphate adsorption onto schwertmannite involves the exchange of structural sulfate by phosphate as well as phosphate adsorption via complexation by OH-groups. In accordance, phosphate adsorption is highly dependent on the way sulfate is bound in schwertmannite, and this will also influence the rates of schwertmannite transformation into goethite. To analyze the mode of phosphate adsorption and the transformation of phosphate-reacted schwertmannite, FTIR and XRD were employed. The kinetics and extent of phosphate adsorption onto schwertmannite was studied in batch adsorption experiments, using photospectrometric methods for the analysis of phosphate, sulfate and Fe.

Characterization of water treatment residues (WTR) to be employed in P-TRAP systems

Different types of water treatment residues (Fe-oxide sludges, pelletized Fe-oxide sludge, Fe-oxide coated sands) relevant for P-TRAP systems were obtained from AquaMinerals. ESR7 currently characterizes selected WTRs for their physicochemical properties (elemental and mineralogical composition, specific surface area), as a basis for continuing laboratory work on the structure, reactivity and aging of these solids and field studies on their use in soils, sediments and water filters. ESR9 measured phosphate adsorption isotherms on iron-coated sands that will be used in sediment incubation experiments, and ESR2 selected suitable WTR for use in experiments on P availability in soils.

Characterization of Fe and P in soils and sediments

Contacts between Utrecht University and Bayreuth have been established to transfer skills from UU regarding the solid-phase characterization by sequential extraction, and ESR11 will visit Utrecht in March 2020 to learnt the respective methods from ESR9. The same sequential extraction protocol will then be used for the characterization of sediments by ESR9 and ESR11. ESR2, with inputs from ESR9, formulated MS5, a compilation of protocols for the characterization of Fe and P in soils and sediments using chemical extraction techniques.

Task 4: Characterising solid-bound Fe and P with state-of-the-art microscopic and spectroscopic techniques (EAWAG, UU, UNIVIE, UNIMAN)

> *Spectroscopic and microscopic techniques, including synchrotron-based X-ray spectroscopy will be applied to investigate the association of Fe and P down to atomistic level.*

Spectroscopic techniques of interest within P-TRAP include synchrotron-based X-ray absorption spectroscopy (XAS) for Fe and P speciation, Mössbauer spectroscopy for Fe phase characterization, Raman and Fourier-transform infrared (FTIR) spectroscopy for solids identification and the study of sorbed ions such as phosphate. Furthermore, X-ray diffraction (XRD, mineralogy) and X-ray fluorescence (XRF; elemental composition) are of interest. Using micro-focused synchrotron radiation, also spatially resolved analyses may be performed on heterogeneous samples.

In terms of electron microscopy techniques, both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) may be of interest within P-TRAP, including their combination with energy-dispersive X-ray detection (EDX) for elemental analysis, depending on the spatial scale of the features of interest. Furthermore, TEM also offers the possibility for spatially resolved sample characterization for structure (SAED) and speciation (EELS).

First synchrotron experiments were performed in the context of the first experiment of ESR7 on precipitate aging under oxic conditions, as described under Task 1 (Fig. 11). ESR6 familiarized with the use of XRD, Raman and FTIR spectroscopy and electron microscopy, ESR9 gained first experience with Raman and FTIR spectroscopies, and ESR10 optimized the use of Raman spectroscopy for the characterization of vivianite under anoxic conditions and without irradiation artefacts, as described under Task 3. Within the second year, exchange among the ESRs will allow to mutually profit from analytical experiences and competences gained by the different project partners.

Currently, synchrotron beamtime is scheduled for ESR7 in May 2020 and possibly June 2020. During these beamtimes, time will also be available for the characterization of Fe solids relevant in other ESR projects. During the first of these beamtimes, it may also be possible to test experimental setups for time-resolved in-situ analyses on dynamic systems (solids formation or transformation over timescales of hours). Eawag (ESR7) and UU (ESR6) currently also submit proposals to various synchrotron facilities to apply for beamtime, in order to ensure continuing access to XAS as a key speciation technique.

1.1.4 WP 4 – Training

WP 4 involves all beneficiaries and non-academic partners of P-TRAP. This work package is led by UBT, in collaboration with the UU.

1.1.4.1 Executive summary WP 4

All activities scheduled in WP4 have started and are on track, all beneficiaries and several partner organisations (AquaMinerals, BayFor) are actively involved. Within the first reporting period one deliverable was due, D4.1 - Transferable Skills Training Course 1 (TSTC1). The ESRs were introduced to their individual projects and prepared their CDPs for short and long term.

1.1.4.2 Progress summary per WP partner

All beneficiaries were involved in the local and network-wide training program and had the same tasks within the first reporting period, i.e. I) invent the training needs and wishes by setting up individual CDPs, II) introduce the ESRs to the local training activities, and III) actively participate in the network-wide training activities. UBT organised the first Transferable Skills Training Course (TSTC1), which has been held in January 2020 and reported as deliverable D4.1. The CDPs will be compiled to deliverable D4.4, due in project month 14.

1.1.4.3 WP 4 - Task Report

Task 1: Organise local training

> *Organise local training through CDPs comprising training activities provided by the host institutions with a focus on technical, scientific and generic skills which reflect the methodological expertise of each beneficiary.*

Each host institution introduced their ESR to the scientific environment, so that they get acquainted with it. The ESRs spent their first months to familiarize with their study topics, experimental design and first laboratory work, supported by their supervisors and co-supervisors. Based on their background and the requirements of their individual projects, the ESRs prepared their CDPs and discussed them at the 1st Annual Meeting. More information is given in Chapter 3 of this report and the deliverable D4.4 which is a compilation of all CDPs of the first year.

Task 2: Coordinate network-wide training

> *Coordinate network-wide training focusing on transferable skills, complementary scientific competences, activities enforcing the interdisciplinary qualification and secondments to both the non-academic and academic sector.*

A) TSTC1 - Being a scientist in the 21st century

The first training course of P-TRAP was held in association with the 1st Annual Meeting in Bayreuth, Germany in January 2020. Both, the training and the meeting was hosted by UBT.

The initial planning was to held the training course in project month 9. Due to the late start of several ESRs the training schedule had been slightly re-arranged (agreed on during the 1st P-TRAP teleconference, held 17th of July 2019), and the TSTC1 was shifted to project month 11.

The aim of TSTC1 was to prepare the ESRs for their upcoming function as Early Stage Researcher, being a role model for a scientist operating in a diverse research environment and to bear societal responsibility, as excellence in research alone does not suffice to guarantee the ESRs' success in the future and does not fulfil society's expectation on scientists.

Fig. 17: Participating ESRs, **Row above (from left to right):** Victoria Barcala (ESR3, DELTARES), Ville Nenonen (ESR7, EAWAG), Mingkai Ma (ESR6, UU), Rouven Metz (ESR10, UNIVIE), **Row below (from left to right):** Karel As (ESR9, UBT), Tolulope Ayeyemi (ESR8, US), Rochelle Saracanlao (ESR2, KULeuven), Melanie Münch (ESR11, UU), Oleksandr Bolielyi (ESR4, GEOS)

Specific emphasis was given to communication skills and ethical topics such as research integrity. As this training was the first occasion for the ESRs to meet in person, a dedicated icebreaker session was implemented. During this icebreaker the ESRs had the opportunity to get to know each other in an informal way. Furthermore, the course assisted the ESRs in identifying their training needs and the opportunities within P-TRAP to achieve their learning goals. This was also in the context of the Career Development Plan discussions during the associated 1st Annual SB Meeting afterwards.

Next to the theoretical part, TSTC1 also included an excursion to the waste water treatment plant of Bayreuth as practical part in the context of P-TRAP.

More details are given in deliverable D4.1. Besides this, a blog about the training is available on the P-TRAP website (https://h2020-p-trap.eu/2020/01/23/our-first-get-together/).

B) Secondments

Each ESR has to execute 2 – 3 secondments at academic and non-academic partners, aiming on inter-sectoral knowledge transfer (IKT), and improvement of capabilities to work in different environments and professional networks (ESAS – Exchange of scientific methods, approaches and/or skills). Due to the late start of several ESRs the initial schedule needed to be adjusted (see Table 2) to ensure the secondments being meaningful for the projects.

Table 2: Overview of executed and planned secondments

ESR nr., name, start month, host	Co-supervisor	Secondment hosts	Due date (PM)	Executed / Planned
ESR 1 Xingyu Liu (13) UBT	KULeuven	GEOS	32-34	As the ESR started just 1 March 2020 no secondments have been planned yet.
		UNIMAN	21-22	
		DELTARES	16	
ESR 2 Rochelle Saracanlao (9) KULeuven	UNIVIE	GEOTEAM	33-35	Nov.2021–Jan.2022, replaced to FERTIBERIA
		UNIVIE	27-28	May-June 2021
		EAWAG	14	postponed
ESR 3 Victoria Barcala (8) Deltares	UU	ARCADIS	21-23	2021
		UU	13-14	April - May 2020, but probably postponed
		KULeuven	29	2022
ESR 4 Oleksandr Bolielyi (10) GEOS	UBT	AQUAMIN	31-34	Sep.-Dec. 2020
		UU	10-11	postponed
		US	19	Not yet planned
		UBT	extra	July-August 2020
ESR 5 Lordina Eshun (9) UNIMAN	US	FERTIBER	25-27	Not yet planned
		EAWAG	19-20	Not yet planned
		US	11	October 2020
ESR 6 Mingkai Ma (10) UU	EAWAG	AQUAMIN	27-29	Not yet planned
		UNIVIE	10-11	Nov.-Dec. 2020
		UBT	20	August-Sep. 2021
ESR 7 Ville Nenonen (8) EAWAG	KULeuven	GEOS	34-36	Not yet planned
		DELTARES	14-15	June-July 2020
		KULeuven	23	June 2020
ESR 8 Tolulope Ayeyemi (12) US	UNIMAN	GEOTEAM	31-33	Not yet planned
		UNIVIE	17	July 2020
		KULeuen	21-22	Not yet planned
ESR 9 Karel As (7) UBT	UU	WATERNET	32-34	Not yet planned
		UNIMAN	28-29	October 2020
		UU	20	March 2020
ESR 10 Rouven Metz (7) UNIVIE	UU	FERTIBER	25-27	
		UU	31-34	
		EAWAG	17	
ESR 11 Melanie Münch (11) UU	UBT	WATERNET	27-29	Not yet planned
		UNIMAN	10	October 2020
		UBT	19-20	September 2021

1.1.5 Administrative Work Packages WP 5, WP 6, and WP 7

The administrative work packages (Management, Dissemination, and Ethics) are led by the coordinator (UU). Tasks and progress are described in detail in Chapter 4.

1.2 Deliverables

Within the first reporting period 9 deliverables were due, mainly administrative deliverables (Table 3).

Table 3: overview of the project deliverables and their actual status

Name / description	WP	Lead	Due date	Actual status
D1.1: Novel granular materials and characterisation of their properties	WP 1	GEOS	August 2021	Work started, see Task 1 (WP19
D1.2: Design of P-TRAP system and operating intstructions	WP 1	GEOS	February 2022	This deliverable builds on the outcomes of D1.1. Work will start when sufficient information is available from D1.1
D1.3: Guidelines and recommendations for retaining and recovering Fe-bound P in drainage systems	WP 1	DEITARES	June 2022	Not started yet.
D1.4: Compendium on possible pathways to convert P-containing Fe(III)oxides into vivianite	WP 1	UNIMAN	June 2022	This work has started, but is still in its initial stage.
D1.5: Guidelines and instructions for the application of Fe and P containing solids for soil amelioration	WP 1	US	August 2022	Not started yet.
D2.1: Reports coupling of Fe and P dynamics in lakes	WP 2	UBT	February 2021	Work in progress (cf. task 1)
D2.2: Strategy for achieving long-term P burial in lake sediments by Fe addition	WP 2	UU	February 2021	Work in progress (cf. task 3)
D2.3: Report on binding dissolved P by adding Fe-containing byproducts	WP 2	UU	October 2021	Work in progress (cf. task 2)
D2.4: Report on long-term effects of Fe addition to lakes	WP 2	UU	June 2022	First surveys started
D2.5: Guideline and instructions for using by-products of water treatment for lake restoration	WP 2	UBT	June 2022	Not started yet
D3.1: Kinetic models for the transformation of P containing Fe phases	WP 3	EAWAG	February 2022	Not started yet
D3.2: Report on the fate of P during Fe phase Transformations	WP 3	UNIVIE	June 2022	Not started yet
D4.1: Transferable Skills Training Course (TSTC)1	WP 4	UU	Nov. 2019	Postponed to January 2020 to ensure all ESRs can participate, associated to 1st Annual Meeting, deliverable report submitted and approved
D4.2: Science School 1	WP 4	UU	March 2020	Postponed to July 2020, associated to EU Review Meeting, organised in collaboration with the European Sustainable Phosphorus Platfom (ESPP), in progress
D4.3: TSTC 2	WP 4	UU	March 2020	Postponed to July 2020, associated to EU Review Meeting, in progress
D4.4: Career Development Plan	WP 4	UU	April 2020	All ESRs have received a template for their CDPs and discussed them with their

				supervising team at the 1st Annual Meeting (see D5.6)
D4.5: Research log & Training log	WP 4	UU	April 2020	A draft implementation set-up has been discussed by the ESRs at the 1st Annual Meeting, in progress
D4.6: TSTC3	WP 4	UNIVIE	August 2020	Not started yet
D4.7: Science School 2	WP 4	KULeuven	March 2021	Not started yet
D4.8: TSTC4	WP 4	KULeuven	March 2021	Not started yet
D4.9: TSTC5	WP 4	DELTARES	August 2021	Not started yet
D4.10: Secondments	WP 4	UU	February 2022	Due to the late start of several ESRs the initial secondment plan needs some adjustments to ensure them being efficient and effective. The first secondments have been discussed at the 1st Annual Meeting and will be executed in the 2nd reporting period. An overview of the actual planning is given in Table 2.
D4.11: TSTC6	WP 4	UNIMAN	March 2022	Not started yet
D4.12: Science School3 / Stakeholder Workshop	WP 4	EAWAG	March 2022	Not started yet
D5.1: Implementation meeting	WP 5	UU	March 2019	Held, Deliverable report approved
D5.2: Final Consortium Agreement	WP 5	UU	April 2019	Submitted, CA approved
D5.3: Supervisory Board of the network established	WP 5	UU	April 2019	Deliverable report approved
D5.4: Communication platform established	WP 5	UU	April 2019	Deliverable report approved
D5.5: Data management plan	WP 5	UU	July 2019, postponed Feb. 2020	Postponed to include ESRs contributions, in progress
D5.6: 1st Supervisory board meeting	WP 5	UU	Nov. 2019	Postponed to January 2020, associated to TSTC1 to ensure all ESRs can participate
D5.7: Contract signed with ESRs	WP 5	UU	Feb. 2020	All ESRs selected, start dates between September 2019 and March 2020
D5.8: Progress Report	WP 5	UU	March 2020	This report, submitted
D5.9: SB meeting 2	WP 5	UU	August 2020	Will be held in July 2020 in association with the EU Review Meeting.
D5.10: SB meeting 3	WP 5	UU	August 2021	Not started yet
D5.11: SB meeting 4	WP 5	UU	August 2022	Not started yet
D6.1: Public-engagement strategy	WP 6	UU	April 2019	Deliverable submitted, to be updated
D6.2: E-learning module	WP 6	UU	April 2022	Not started yet
D6.3: Final conference	WP 6	UU	August 2022	Not started yet
D6.4: Discovery day	WP 6	UU	January 2023	Not started yet
D6.5: E-newsletter (in English)	WP 6	UU	December 2021	Not started yet
D6.6: Model tools	WP 6	UBT	February 2023	Not started yet
D6.7: End-user manual	WP 6	UU	February 2023	Not started yet
D6.8: Potential inputs for Policy Feedback	WP 6	UU	February 2023	Not started yet
D7.1: EPQ requirements no.1	WP 7	UU	Feb. 2020	In progress

1.3 Milestones

Within the first reporting period the consortium achieved all 10 envisaged milestones, the reports about this are in progress. At the 1st Annual Meeting the consortium discussed and planned the upcoming milestones for the second period.

Table 4: overview of milestones in the project and their actual status

Name / description	WP Associated deliverable	Lead	Due date	Actual status
MS1: Recruitment of ESRs *Recruitment of ESRs complete*	WP4 / WP5 D5.7	UU	Feb. 2020	All ESRs selected, start dates Sep. 2019 to March 2020, D5.7 approved
MS2: Structure data base data management *Specifications, design and technical structure of the data base has been defined*	WP5 / WP6 D5.5	UU	July 2019, postponed Feb. 2020	Postponed in agreement with PO to include ESRs contributions, in progress
MS3: Selection of suited lakes *Selection of suited lakes finished*	WP2 /	UU	Nov. 2019	Milestones achieved, report submitted
MS4: Selection of relevant soil types *Selection of relevant soil types for which the effect of adding P-containing Fe phases will be tested have been identified*	WP1 /	US	Nov. 2019	Milestone achieved, report submitted
MS5: Protocol solid characterisation *A procedure for standard characterization of Fe and P phases in soils and sediments to be shared by all partners has been established*	WP1 – WP3 /	KU Leuven	Nov. 2019	Milestone achieved, report submitted
MS6: Monitoring strategy lakes *A strategy for monitoring the P and Fe dynamics in lakes will be developed including type of sampling, measured parameters and frequency*	WP2 /	UBT	Feb. 2020	Milestone achieved, report to be submitted
MS7: Specification of sorbents *The required specification of novel granular materials to trap P in drainage systems has been delineated.*	WP1 /	GEOS	Feb. 2020	Milestone achieved, report submitted
MS8: Sites selected for drainage systems *In collaboration with the Partner Organisations suitable sites in drained areas are selected for testing new technologies for retaining Fe-bound P.*	WP1 /	DELTARES	Feb. 2020	Milestone achieved, report to be submitted
MS9: Specification of quantitative models *A framework has been designed which defines the involved processes, the required temporal and spatial resolution of the models*	WP1 / WP2 /	UBT	Feb. 2020	Milestone achieved, report to be submitted
MS10: Targets microbial conversion *The targets for the microbial conversion of P-containing Fe(III)oxides in terms of expected characteristics of the input material and the expected products.*	WP1 /	UNIMAN	August 2020	Preliminary work started
MS11: Proof of principle of P-TRAP systems *The requisites of the P-TRAP system to retain dissolved P in drainage system have been*	WP1 /	GEOS	August 2020	Preliminary work started

specified and constrain the design of the system				
MS12: Strategy Fe addition lakes *Based on measurements and model calculations a suitable strategy for adding Fe-containing by-products to lakes has been developed.*	WP2 /	UU	August 2020	Work in progress
MS13: Implementation plan P-TRAP system *A detailed plan to implement the P-TRAP system in a drained area has been made*	WP1 /	GEOS	February 2021	Not started yet
MS14: Implementation plan lake restoration *The planning for testing the addition of Fe-containing by-products to improve water quality in lakes has been finalized.*	WP2 D2.2	UBT	February 2021	This task depends on data to be generated in laboratory experiments and has not been addressed so far.
MS15: Implementation plan soil fertilisers *A plan to demonstrate the suitability of Fe-containing phases as soil fertilisers or conditioners has been established*	WP1 /	US	February 2021	Not started yet
MS16: Validated management assessment completed *Validated management assessment of lakes completed with respect to the restauration activities*	WP2 / WP3 /	UU	June 2022	Not started yet
MS17: All recruited fellows enrolled in PhD programme *All recruited fellows enrolled in PhD programme*	WP5 D5.7	UU	Feb. 2020	All ESRs selected, start dates between September 2019 and March 2020, D5.7 approved
MS18: Project check *Meeting between REA and consortium*	WP5 /	UU	August 2020	The meeting is scheduled 16 July 2020, associated to the 1st P-TRAP school, TSTC2, and a SB meeting

1.4 Progress of the individual ESRs

All ESRs have been started their contracts, however, several just a few weeks ago. Thus, the focus of the first period was getting acquainted with the project, familiarize with their study topics, experimental design and first laboratory work. All ESRs have to report their progress regularly, at least once a year, based on a template provided by the management. The individual ESR progress reports are part of the P-TRAP reporting (see attachment).

2. Recruitment

The recruitment strategy, the organization of the recruitment process, and the selected candidates have been described in detail in deliverable D5.7, submitted in February 2020.

2.1 Recruitment strategy

Based on experiences and requirements of the consortium, a decentralized recruitment strategy had been chosen. Although P-TRAP officially started in March 2019, the recruitment procedure started with launching the website in February 2019 to ensure an efficient and timely recruitment. The aim was to recruit all ESRs ideally within the first six months of the project until September 2019.

The following recruitment strategy had been implemented:

- Each beneficiary was responsible for the advertisement of and the recruitment on its own ESR position, supported by general advertisements launched by the coordinator. All advertisements were redirected to the project website, which was kept up-to-date by the coordinator regarding the positions. On the website a detailed description of the positions and requirements were given, also contact details of the respective supervisors.
- For administrative and monitoring reasons, the applicants had to apply directly via the electronic submission system of the Human Resource (HR) department of Utrecht University, or via the electronic submission systems of those partners who have their own system available (EAWAG, DELTARES). The application channels and deadlines were clearly indicated in the advertisements. Applications via direct email to the supervisors were not encouraged, but accepted.
- The coordinator collected all applications that came in via the electronic submission system of the Human Resource (HR) department of Utrecht University. For each ESR position an individual folder was created, with access only given to the responsible PIs and the coordinator. By implementing this procedure wide-spread applications which did not specifically address one of the positions were avoided. The applications were treated following the national and EU rules for protecting privacy. Data were deleted after the recruitment procedure was finished.
- For monitoring reasons, the coordinator got access to the electronic submission systems of the Human Resources department of EAWAG. For DELTARES this option was not available, but the Human Resource department of DELTARES informed the coordinator on request about the progress and the gave an overview of applications and their implemented recruitment procedure.
- Each beneficiary was responsible to ensure the implementation of an open, transparent and comparable procedure following the European Code of Conduct. To ensure that all beneficiaries have the necessary information of these procedures, the *“General Principles and Requirements for the Code of Conduct” (*http://ec.europa.eu/euraxess/index.cfm/rights/codeOfConduct) were provided by email (28 January 2019) and an overview was given during the Kickoff Meeting (13-14 March 2019). The document was also handed out as a hard copy during the Kickoff Meeting, and is also available on the internal part of the P-TRAP website (since 10 March 2019).
- The beneficiaries were solely responsible for the compliance with the EU eligibility rules and the selection of the best candidate, but in case of questions they were supported by the coordinator and the EU National Contact Points. Due to the planned intense collaboration between some beneficiaries and the non-academic mentors, dedicated mentors were included in the selection procedure.
- All applications that were received until the deadline of 1 May 2019 got full consideration. In the advertisements it had been mentioned, that the given deadlines in the job descriptions marked the start of the evaluation procedure followed by the selection procedure. Although the vacancy portals for individual positions were closed after the deadline, eligible applications received via email were taken in consideration until the positions were filled.

2.2 Advertisement

The vacant positions were advertised widely – local, national, and international – to ensure a maximum of visibility and awareness, both individually and grouped into a general P-TRAP project advertisement. The advertisement started with the launch of the website in February 2019 and closed finally with the recruitment of the last ESR in September 2019. Due to the resignation of ESR1 because of personal reasons, the advertisement was reopened for this position, following the same procedure as described below.

The positions were advertised both individually by the participants or the coordinator for the whole project, using several platforms, e.g.:

- International scientific internet-based job platforms such as
  - EURAXESS (e.g. https://euraxess.ec.europa.eu/jobs/384116)
  - EGUjobs (https://www.egu.eu/jobs/2315/)
  - AcademicTransfer (https://www.academictransfer.com)
  - EarthWorks (http://www.earthworks-jobs.com/geoscience/utrecht19031.html)
- Project website (https://h2020-p-trap.eu/vacancies/)
- Subject-related mailing lists:
  - Individual project mailing lists of beneficiaries, e.g H2020 LANMARK project distribution list (18 partners)
- Social media platforms such as Twitter (e.g. #H2020_P-TRAP: https://twitter.com/h2020_PTRAP/status/1113426203636113408?s=09, #MSCAjobalert: https://twitter.com/search?q=%23MSCAjobalert%20p-trap&src=typd), ResearchGate (https://www.researchgate.net/project/P-TRAP), and LinkedIn (https://www.linkedin.com/feed/update/urn:li:activity: 6514841142293598209/)
- Individual institutional websites or bulletin boards of the respective beneficiaries
- Recruitment poster - provided by the coordinator -, placed strategically at the host institutions, at conferences as e.g. the EGU2019 (https://meetingorganizer.copernicus.org/EGU2019/EGU2019-13576.pdf), and by interested colleagues
- Personal scientific networks of the consortium members

The advertisements of individual projects were standardized as much as possible to ensure, that all applicants will get the same amount of information. This included a

- Short description of the project
- Description of working conditions and entitlements, including career development prospects
- Short description of the selection process (selection criteria, selection committee, interview conditions, timeline, ...)
- Deadline for application
- Contact for applicants to get more information about the project

As the positions offered within P-TRAP are highly diverse, the responsible PIs formulated individual criteria for selection based on the direction of the ESR projects. The coordinator consolidated all vacancy descriptions and published them on the project website. To ensure that applicants are aware of the EU eligibility criteria those were also added to the text of advertisement.

For each position, a deadline was set for application, and eligible applications until this date received full consideration. The deadlines marked the start of the evaluation procedure followed by the selection procedure. Although the vacancy portals for individual positions were closed than, late eligible applications were taken into consideration until the positions were filled. In case no suitable candidates were found during the first round, the recruitment procedure could have been re-opened.

For ESR 5 (UNIMAN) the internal procedure was not followed as requested, so the position had to be advertised also on national level after closing the international advertisement.

2.3 Selection criteria

The concept of P-TRAP is to combine different methods, methodologies and approaches to tackle two urgent interlinked global problems: the potential shortage of phosphate for producing agricultural fertilizers and the decline of surface water quality up excess of phosphate input. Due to I) the diversity of the ESR projects, II) the requested collaboration within an international consortium, and III) the proposed training programme within P-TRAP the ESRs are expected to have several characteristics, talents and skills respective to their individual project. This includes as well scientific as soft skills, such as:

a) Scientific skills, e.g.

- An excellent master's degree in e.g. geosciences and environmental sciences incl. microbiology, chemistry, ecology, mineralogy, soil sciences, agronomy, process/chemical/environmental engineering, water management,
- Strong background, experience, and proficiency in biogeochemical processes in aquatic and terrestrial environments, environmental chemistry, industrial/waste water treatment, plant physiology
- Experience in laboratory work, measurement techniques such as e.g. spectroscopy, general experimental techniques in aquatic/soil/plant sciences, and data analysis tools
- Experience in fieldwork
- Experience in geochemical / hydrological modelling
- Interest and skills in deterministic/diagenetic modelling and programming
- Computational skills, programming, and statistics

b) Soft skills, e.g.

- Interested and innovative, passionate, enthusiastic, and highly self-motivated to work with state-of-the-art environmental research
- Analytical thinking abilities
- Eager to develop multidisciplinary skills
- Excellent written and spoken English language skills
- Experience in scientific writing, such as publications, essays or equivalent in English
- Being independent, creative, and able to work collaboratively inside and outside the consortium
- Take responsibility for parts of the research project
- Willingness to travel abroad for secondments and measurement campaigns
- Willingness to present to an international research community
- Excellent team players

Applicants have to demonstrate ability, experience and potential of excellence. EU eligibility - being an Early Stage Researcher and fulfilling the mobility rule - and scientific eligibility were the primary selection criteria, followed by the promise of high training efficacy, and the expected return. A first evaluation of candidates was based on their:

- EU eligibility
- Application letter (e.g. quality of writing and content; reference to advertised position)
- CV (e.g. scientific discipline, general project relevant activities, skills in laboratory and analytical work; in data collection and interpretation)
- diplomas (grades)
- references

Candidates that found not suitable for the project were rejected by the responsible PI or by the HR departments on request of the responsible PIs. Eligible candidates were than ranked for the following procedure. The ranking followed a pre-defined classification of evaluation criteria.

2.4 Interview procedure

The PIs responsible for the recruitment ranked the eligible candidates with support by their selection committee, and shortlisted candidates were invited by email for a first-round interview. The first interviews were mostly held remotely by Skype, and if possible followed by a personal interview at the host location for the most promising candidates. Costs for the interviews were on request reimbursed by the host institutions.

The selection committees were composed of normally 2 to 4 researchers, including the main supervisor and e.g. a member of the research groups, and for some beneficiaries also a representative of the HR department. During interviews, the candidates were asked to present themselves, their background and their interest in the position. Following the interviews, the committees discussed the skills and matching of each candidate regarding the objectives of the positions and ranked them accordingly. The positions were offered to the candidate on the first position, in case a candidate waived the position it was offered to the candidate next on the list.

2.5 Timeline of the recruitment procedure

The consortium strove for finishing the recruitment within the first six months of the project. As this was very ambiguous, the advertisement procedure started already after the Grant Agreement had been signed by announcing the upcoming vacancies locally and in the personal networks. With the launch of the website (February 2019) the application procedure started officially as described above. Although the project is of high relevance and positions were advertised widely, several positions attracted fewer applicants than expected and also the quality - including the eligibility - of applicants was beyond expectations.

Table 5: Timeline of recruitment procedure

	Hosting beneficiary	Start evaluation	Interviews	Candidate selected	Proposed start of employment
ESR1*	UBT	01-05-2019 15-01-2020	May – June 2019 January 2020	June 2019 January 2020	01-10-2019 01-03-2020
ESR2	KULeuven	01-05-2019	June 2019	July 2019	15-11-2019
ESR3	DELTARES	01-05-2019	May – June 2019	June 2019	14-10-2019
ESR4	GEOS	01-05-2019	July – August 2019	September 2019	01-12-2019
ESR5**	UNIMAN	01-05-2019 27-10-2019	June – July 2019 October 2019	July 2019 October 2019	01-11-2019
ESR6	UU	01-05-2019	June – September 2019	September 2019	01-12-2019
ESR7	EAWAG	01-05-2019	May – June 2019	June 2019	01-10-2019
ESR8	US	01-05-2019	August 2019	September 2019	1-10-2019
ESR9	UBT	01-05-2019	May – June 2019	June 2019	03-09-2019
ESR10	UNIVIE	01-05-2019	May – June 2019	June 2019	01-09-2019
ESR11	UU	01-05-2019	May – June 2019	June 2019	01-01-2020

*Position was re-opened for 4 weeks (13.12.2019 till 15.01.2020), candidate selected 30.01.2020

** Position was re-opened for 4 weeks (start 27.09.2019), candidate was selected 30.10.2019

2.6 Applications

The consortium received more than 700 applications by 455 individual applicants in total. The applicants originated from 72 countries (Fig. 18). 18 % came from Europe (western and eastern), whereas the majority belonged to the Asia-Pacific group (55 %) and Africa (23 %) (Fig. 19), the grouping follows the United Nations classifications (http://www.un.org/depts/DGACM/RegionalGroups.shtml).

When considering the country of residence, the amount of individual applicants staying in Europe almost doubled compared to the country of origin (32 %), indicating international experience in their field of interests.

Although applications from more than 70 countries were received, a few countries dominated the picture, especially the number of applicants from the Asia-pacific group (Fig. 20). More the 60 % of the applicants originated from in total 10 countries, and almost three quarters of them came from Iran, India, China or Pakistan. Only Italy as a Western European Country was represented within the top 10 countries of origin. Spain followed on place 11.

2/3rd of the applicants were clearly eligible, only 1/3rd could not be considered. This was mainly due to not fulfilling the EU criteria of being an Early Stage Researcher (ESR) or incomplete documentation so that the eligibility could not be concluded (Fig. 21).

Please note that as not for all applicants all information was given in the applications, as e.g. the country of origin, gender, or age, thus the absolute numbers in the figures can differ.

The total number of applications differed significantly between the offered positions, also the number of eligible applications (Fig. 22). On an absolute level, most applications came in for the position in Switzerland, but also for Belgium, Spain and the Netherlands. The number of applications for the position in Germany is higher due to the re-opening and is therefore less representative.

The number of positions to apply to was not restricted. However, most applicants applied for just one (78%) or two positions (10 %), 10 % applied for 3 - 5 positions, and only 3 % for 7 or more positions.

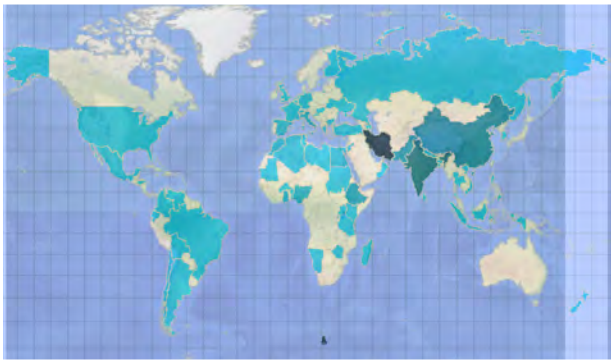

Fig. 18: geographical overview of applicants countries (Map: geo.dianacht, https://geo.dianacht.de/makemap/index.php), background: natural earth (http://www.naturalearthdata.com)

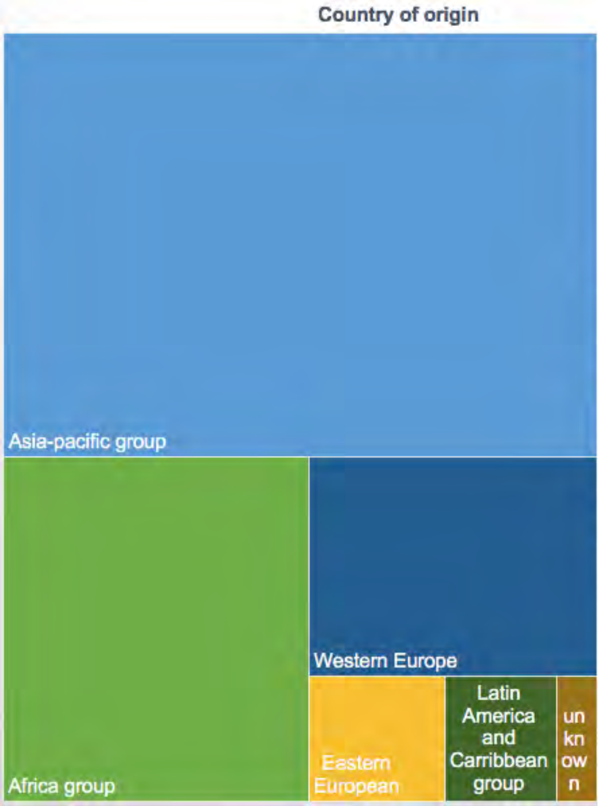

Fig. 19: Country groups of origin (applicants) http://www.un.org/depts/DGACM/RegionalGroups.shtml

Regarding gender, the number of applications by male was slightly higher with 56 %. This picture differs within the country groups (Fig. 24), where the ratio male:female changed e.g. to 3:1 for the applicants from the Africa group or to 1:3 in the group of applicants from Eastern Europe. Relatively, the amount of ineligible applications was almost equally distributed between male and female.

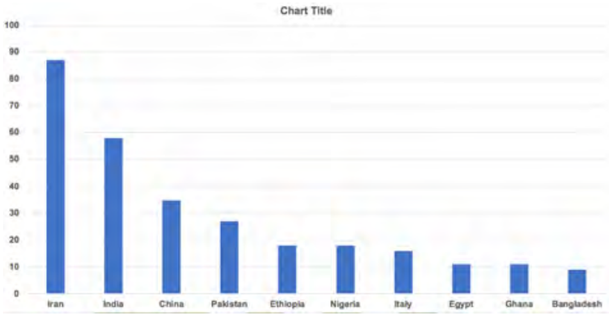

Fig. 20: Main countries of origin (applicants)

As expected due to the EU eligibility rule regarding career stage, most applicants were between 26 to 30 years old (50 %) or 31 to 35 (24 %). Only 7 % were 25 years old or younger.

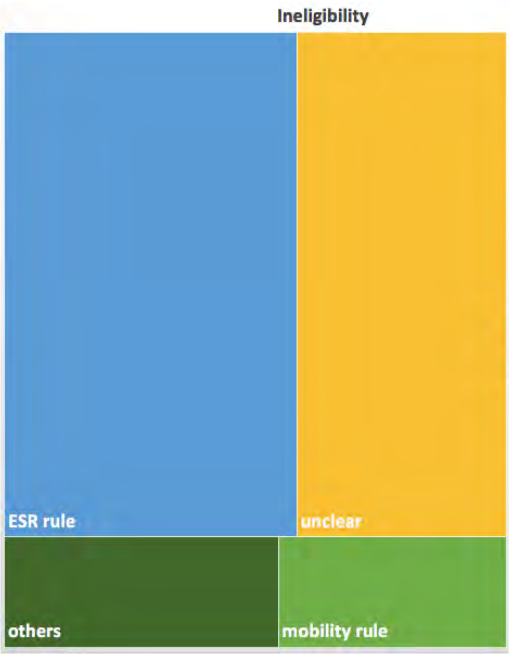

Fig. 21: Reasons for ineligibility

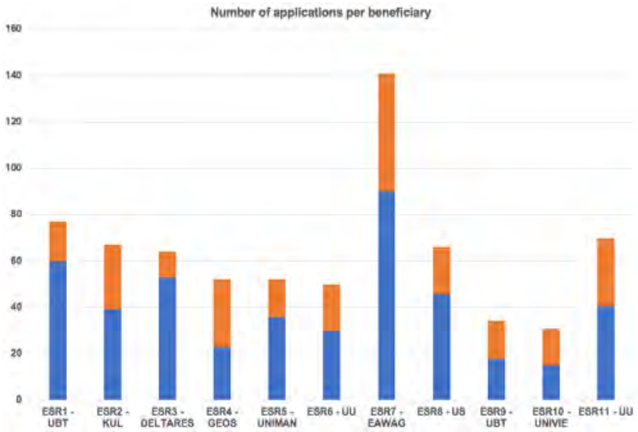

Fig. 22: Number of total applications per position, blue coloured columns indicates eligible applications, orange indicates ineligible or unclear applications. Please note: as applicants could apply for more than one position, the numbers can differ from numbers based on applicants.

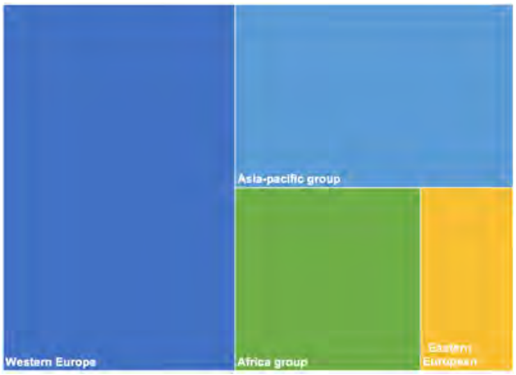

Fig. 23: Country groups of selected ESRs

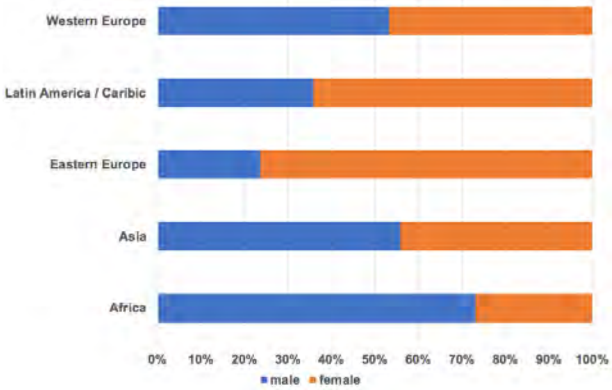

Fig. 24: Gender distribution of applicants sorted by country groups, blue: male, orange: female

2.7 Selected candidates

As described above, P-TRAP is a highly complex project, requiring candidates that are expected to have several characteristics, talents and skills. Although formally eligible, a high number of applicants did not show the necessary experience, educational background or required skills for the project and those applications could unfortunately not being considered.

The majority of the more than 50 selected candidates for interview were still originating from Asia and Africa (45 %), but not as clearly dominating as in the overall group of applicants.

Regarding gender almost 60 % of the invited applicants were female, and also the gender ratio of the selected ESRs shows 6 female and 5 male.

Although the majority of applications were received from countries belonging to the Asia group, particularly India and Iran, this is not mirrored in the country distribution of the selected ESRs (Fig. 23, Table 6). The employed P-TRAP ESR group is highly divers, coming from 10 different countries. Half of the ESRs originates from Europe, particularly Western Europe, and the other half from the Asia and Africa groups.

Table 6: Selected ESRs, their supervision and secondments

ESR	Host beneficiary	ESR Name	Country of Origin	Gender	Co-supervisor	Secondments
ESR 1*	UBT	Xingyu Liu	China	Female	KULeuven	GEOS UNIMAN DELTARES
ESR 2	KULeuven	Rochelle Ioie Saracanlao	Philippines	Female	UNIVIE	GEOTEAM UNIVIE EAWAG
ESR 3	DELTARES	Victoria Barcala	Uruguay	Female	UU	ARCADIS UU KULeuven
ESR 4	GEOS	Oleksandr Bolielyi	Ukraine	Male	UBT	AQUAMIN UU US
ESR 5	UNIMAN	Lordina Eshun	Ghana	Female	US	FERTIBER EAWAG US
ESR 6	UU	Minkai Ma	China	Male	EAWAG	AQUAMIN UNIVIE UBT
ESR 7	EAWAG	Ville Nenonen	Finland	Male	KULeuven	GEOS DELTARES KULeuven
ESR 8	US	Tolulupe Ayeyemi	Nigeria	Female	UNIMAN	GEOTEAM UNIVIE KULeuen
ESR 9	UBT	Karel As	Netherlands	Male	UU	WATERNET UNIMAN UU
ESR 10	UNIVIE	Rouven Metz	Germany	Male	UU	FERTIBER UU EAWAG
ESR 11	UU	Melanie Münch	Switzerland	Female	UBT	WATERNET UNIMAN UBT

* First selected ESR: Elmira Akbari, Iran

3. Career Development Plan

The Career Development Plan (CDP) is a deliverable of the project (D4.4), and as described in the Grant Agreement it is mandatory that ESRs undergo formal assessment by the supervisor and co-supervisor once per year. The formal yearly assessment meetings will be associated to the annual meetings and documented in an updated Career Development Plan.

The CDPs are confidential and are only for the members of the consortium and the Commission Services. The aim of the Career Development Plan (CDP) is to help PhD students to define and update their professional projects on the short (1yr) and longer terms and to have a strategy to acquire the missing skills to fulfil their objectives.

At the beginning of the project a template Career Development Plan (CDP) had been created, based on the EU template and adjusted to the project. Each ESR was provided with the template and was requested to prepare her / his individual CDP. The first versions of the individual CDPs were submitted as deliverable D4.4.

At the 1st Annual Meeting, held in month 11, the CDPs were discussed between the ESR, the supervisors, co-supervisors and if possible with the host of the first secondments. Each discussion was scheduled for 45 min. to ensure enough time for discussions and a proper planning directly from the start.

4. Overall management of P-TRAP

The management of P-TRAP is organised based on the Grant Agreement and the Consortium Agreement. The project structure and the management of it will follow the approach described in Chapter 3.2 of the GA, Part B, and the CA. The GA was provided as a hardcopy to all participants of the Kickoff Meeting and is also available in digital form for all participants on SurfDrive, accessible via the internal part of the project website. The Consortium Agreement (CA), which had been finally signed mid-May 2019, is also available on that platform. These two documents provide the basis for the management of P-TRAP.

The project management, implemented by the UU as coordinating beneficiary and organized within WP5, provides scientific and administrative coordination of the project according to the EU requirements and facilitates communication within the consortium and also between the consortium and external stakeholders, e.g. the European Commission. The project management is responsible for regular reporting to both. In close collaboration with the consortium the project management will ensure the dissemination of results inside and outside the consortium and also the maintenance of the website for internal and external exchange of information. The tasks as described for WP5 are:

Task 5.1: Establishing a management structure according to the GA

Task 5.2: Development of a Consortium Agreement (CA)

Task 5.3: Ensure proper operation of training activities

Task 5.4: Provide IT solutions to operate ESRs´ training and research logs

All tasks started officially in project month 1 (March 2019), are on track and ongoing until the end of the project.

The overall management of P-TRAP also includes the dissemination and exploitation activities, organised in WP 6 (see Chapter 4.1.4), as well as the ethical aspects, organised in WP 7.

The ethical aspects are focusing on the collection of samples in natural environments and to some extend to the performance of experiments in natural environments. The responsible PIs will ensure to obtain all necessary authorisations for sampling and performing experiments in natural environments. The respective PIs are also responsible for compliance of all activities with the national and EU legislation on nature conservation and pollution control. This is described in more detail in deliverable D7.1.

4.1 1st Reporting Period

Within the first reporting period of P-TRAP only small changes or adjustments were made, with no significant impact on the project, neither scientifically nor administratively.

4.1.1 Risk assessment and faced difficulties

In the first reporting period we faced two risks, but with no significant impact on the project. A detailed overview of possible risks is described in Table 1.3.5 of the Grant Agreement.

Risk 1: ESR1 decided after 2 months of employment to resign due to personal reasons. Thus, the recruitment procedure was re-opened. A new candidate was selected in February 2020 (month 12) and started in March 2020.

Risk 2: Due to the resignation of ESR1 some milestones are slightly delayed, but are in progress. The delay has no significant impact on the project in general. D5.5 (Data management plan) had been postponed in agreement with the project officer, as the consortium wanted to include the ESRs in the setup. Data management was one topic on the 1st Annual Meeting and it´s coordination is ongoing.

Risk 3: The ESR recruitment took longer than expected, but was still on schedule. In project month 8, respectively month 12 (see Risk 1) all ESRs were selected. However, the initial planning of the secondments started already from month 6 of the project, as this was the envisaged begin date of the ESRs in the proposal. Therefore, the secondment schedule will be structurally postponed.

Difficulties were faced on organisational administrative level. Several ESRs received legal documents not in English but only in the country language of the host beneficiaries. The supervisors helped with translations, but it would be desirable to provide legal documents at least in English for international employees. Besides this, the recruitment of ESR5 and ESR8 was delayed because of national recruitment rules and visa issues.

4.1.2 Consortium

The initial consortium has not changed during the first reporting period. All 9 beneficiaries and 7 partner organisations are involved and part of the consortium. Due to the commitment indicated in the proposal some partner organisations were more active in the first reporting period as others, e.g. in participating in the meetings (AquaMinerals) or contributions to training events (BayFor).

4.1.3 Meetings

To foster close collaboration, regular meetings were implemented right from the beginning and on all levels within the consortium. If possible, meeting dates were chosen by consensus (using the date finder “doodle”) to ensure participation of as much partners as possible. In case this is not possible, the meeting organiser decides in agreement with the management. The meeting organisers were asked to prepare minutes from their meetings and provide them to the project management.

I) Consortium Meetings: Within the first reporting period two Consortium Meetings were held, the P-TRAP Implementation Meeting (13 - 15 March 2019), hosted by the coordinator (UU), and the 1st Annual Meeting, hosted by UBT (8 – 10 January 2020). At both events all 9 beneficiaries and 2 out of 7 partner organisations (AquaMinerals and BayFor) participated and showed a high level of commitment and interest in the project.

As the level of experience with H2020 MSCA ITN-ETNs differs within the consortium, the aim of the *Implementation Meeting* was to introduce all participants to the same level of understanding of an H2020 ITN-ETN. Special attention was laid on presenting the administrative requirements and discuss general procedures, e.g. for the submission of deliverables. To ensure sufficient time for those administrative discussions but also for the scientific ones, the meeting was scheduled for 2 ½ days. The beneficiaries were asked to prepare a short presentation introducing themselves and their institution. The agenda included also time slots for discussions of the scientific status and preparatory work, required networking and interactions between the groups to ensure an efficient start of the project. All beneficiaries received a hard copy of the Grant Agreement.

At the end of the first reporting period the *1st Annual Meeting of P-TRAP* was held (8 – 10 January 2020), hosted by UBT. The meeting was held in association with the first Transferable Skills Training Course (TSTC1). Both, the training and the meeting were hosted by UBT with organisational support by the UU.

The initial planning was to held the meeting in project month 9. Due to the late start of several ESRs the meeting had been slightly postponed (agreed on during the 1st P-TRAP teleconference, held 17th of July 2019) to project month 11.

Fig. 25: Participants of the 1st Annual P-TRAP Meeting

The 1st Annual SB Meeting was scheduled for two full days in total and aimed on scientific exchange within the consortium and training of the Early Stage Researchers (ESRs). The consortium consisted of the representatives of the beneficiaries and two of the partner organisations, and included also the ESRs. Beside this, our External Advisory Board (EAB) was invited to participate and provided us with feedback. A summary of the EAB feedback and implementation of the recommendations is given in Chapter 4.1.6.

During the meeting the consortium was updated about the 1st year of the project. The participants discussed and evaluated the progress so far, and prepared the second year. The ESR projects were presented by the ESRs as short pitches and posters. The planning of the upcoming work of the next reporting period focussed particularly on the due deliverables and milestones. An intensive CDP discussion was scheduled for the ESRs together with their supervising team. The discussions were held in parallel groups. ESRs, which were not discussing their CDPs where invited for alternative discussions about the organisation of e.g. training and research logs or the use of social media within the project. The last day was dedicated to consortium related issues such as data management and public relation strategies, and evaluative feedback.

II) 3-monthly tele-conferences: The consortium held two tele-conferences, starting four months after the Implementation Meeting. For the tele-conferences the coordinator provides access to the internet-based platform WebEx. This platform has been proven to be suitable for all participants and will be used in the future. Dates were picked by using the date finder “doodle”, with at least 5 suggestions regarding day and time.

During the tele-conferences the WP leader were asked to give a brief overview about the status of their work packages and the involved partners, and the participants discussed the main relevant issues for the upcoming months, e.g. status of recruitment, presentation of P-TRAP or upcoming administrative tasks as deliverables and their contributions.

III) ESR skype meetings: This topic had been discussed during the 1st Annual Meeting. The ESRs, which have to implement Training and Research logs, decided to held regular and self-organised remote meetings to document their progress regarding training and research. The coordinator provides the internet-based platform WebEx and will receive the minutes of the meetings. The ESRs will exchange information, and discuss relevant issues such as measurements or data exchange. In case input or information is requested from the ESRs, e.g. for planning network events or reporting, this is communicated by the management to the respective ESR chairmen and discussed within the ESR meetings. The ESR group vice versa can request relevant information from the management. A first remote meeting took place 27th of February.

IV) WP meetings: All WP leaders are encouraged to organise regular WP meetings with the PIs involved in their WP. As the WPs have a close email contact and also in combination with the regular 3-monthly tele-conferences, the frequency of dedicated WP meetings will be on request. A first WP leader meeting took place 17 February aiming on a last check regarding the due reporting.

Table 7: overview of P-TRAP meetings

Meeting	Date / Location	Organizer	Invited participants
Implementation Meeting	13 – 15 March 2019 Utrecht, The Netherlands	UU	All project participants
1st Annual Meeting	8 – 10 January 2020 Bayreuth, Germany	UBT	All project participants
Tele-Conferences *	17 July 2019 26 November 2019	UU	Representatives of all beneficiaries and partner organisations
WP Tele-Conferences**	17 February 2020	UU, Respective WP leader	Coordinator, WP leader
ESR Tele-Conferences	27 February 2020	ESRs	ESRs

* Remote using WebEx

** On request of coordinator or WP leader

4.1.4 Communication Activities

4.1.4.1 Communication infrastructure

The communication infrastructure has been described in detail in deliverable D5.4. According to the spatial distribution of the consortium, the day-by-day communication within the consortium is assured mainly remote by email. The chosen communication channels, structure and frequency worked well during the first year, all participants are responsive and engaged, and the management received requested information with only slight delays. Within the consortium all communication channels are available for any participant, the communication lines are short and direct without formal restrictions. The direct communication with the Project Officer as a representative of the EU as funding agency is restricted to the coordinator.

Communication channels are

I) Email, telephone: The main communication channel according to the spatial distribution of the consortium is email. Individual exchange of information will use the institutional email addresses of the participants. Email is also the preferred channel for official project communication to ensure traceability of information and decisions. Beside emailing, phone calls are also be used as communication channel.

II) Web-based board meetings and tele-conferences: Direct and regular exchange between participating groups and boards increases collaboration and reduce the risk of failing of the project. High-frequent face-to-face meetings are not manageable, costly and also causing unnecessary environmental pollution, thus participants are invited to participate in regular remote board meetings. The technical communication tools are WebEx and Skype.

III) Face-to-face meetings: For the consortium the mandatory face-to-face moments are the annual meetings. The meetings are organized by dedicated beneficiaries and communicated via email and the project website. At the annual meetings ESRs should present the progress of their work, meet with (co-) supervisors and mentors, and the consortium will discuss project related issues. Besides this the ESRs will meet on a regular basis during dedicated network training events.

IV) Funding & tender opportunities portal (https://ec.europa.eu/info/funding-tenders/opportunities/portal/screen/home): The *Funding & tender opportunities Portal*, the former *Participant Portal,* is the web portal of DG Research & Innovation and the entry point for electronic administration of EU-funded projects. The *Funding & tender opportunities Portal* hosts the services for managing projects throughout their lifecycle. The coordinator will use the *Funding & tender opportunities Portal* for general project managing. The beneficiaries have to use the EU *Funding & tender opportunities Portal* for individual beneficiary related reporting or documentation issues, e.g. financial reporting or submission of researcher declarations.

V) P-TRAP website: The project website of P-TRAP (Fig. 26, https://h2020-p-trap.eu) serves as a central communication platform within and outside the consortium, and will be used for dissemination of project relevant information, including documents (e.g. GA, CA, deliverables, minutes), templates, and results. Sensible information is password protected and only available for project participants via SURFdrive, a personal cloud service for the Dutch education and research. All participants are encouraged to use the website for information exchange. The website was launched one month before the official start of the project and is maintained by the coordinator, with input from all participants.

P-TRAP involves 9 academic partners and 7 companies in Germany, The United Kingdom, Switzerland, Spain, Belgium, Austria and The Netherlands. The consortium offers 11 PhD positions and is looking for highly motivated candidates, with a strong background in fields requested for the individual projects and excellent English language skills (spoken and written). A unique feature of ETN's is the combination of research and training units, which includes the opportunity to perform secondments of several weeks or months at the facilities of other consortium members. Candidates will benefit from a dedicated training program in the various fields of expertise of the consortium members and also from this network of internationally recognized scientists and private companies. Candidates must be willing to travel abroad for secondments and measurement campaigns, and to present their research to an international research community. As this project requires close collaboration within the consortium, candidates are expected to be team players. MSCA-ETN projects are part of Horizon 2020 and offer attractive salaries and working conditions following the conditions as described in the respective work programs.

As this is an EU H2020 MSCA-ITN-ETN project, the following eligibility criteria needs to be fulfilled and proven:

i) Researchers may be of any nationality, BUT may not have resided or carried out their main activity (work, studies, etc.) in the country of the host organisation they are applying to for

Fig. 26: screenshot of the vacancies of the P-TRAP project website


H2020_PTRAP @h2020_PTRAP · Apr 9
Learn more about @h2020_PTRAP? Join me at #EGU2019, 10.45 at poster X1.116 @UniUtrecht @unisevilla @AquaMineralsNL @deltares @Uni_Bayreuth @LeuvenU @univienna @EawagResearch @ETH @MSCActions @EU_H2020 @NutrientP @arcadisnl @Waternet @TNO_Research

Fig. 27: P-TRAP advertisement on LinkedIn


You
added an update

P-TRAP just started! JOIN US!
Within our new H2020 MSCA ITN-ETN we are searching for 11 enthusiastic PhD students with strong backgrounds in environmental sciences. Interested? More information at https://h2020-p-trap.eu/ #msca #environmentalscience #h2020PTRAP @UtrechtUni @UniVienna #UniBayreuth #EAWAG @OfficialUoM @UniSevilla #KULeuven @Deltares

You
added a project goal
Flux of phosphate (P) from agricultural areas to surface waters is wasting a resource which is becoming scarce and is in conflict with

Fig. 28: Announcements on ResearchGate

Visitors of the website will find general information about the project and its objectives, overviews of relevant scientific results and short report summaries, later also dissemination activities such as blogs, newsletters and fact sheets.

VI) Social media, newsletters, factsheet: Social media such as LinkedIn, Twitter (Fig. 27), or ResearchGate (Fig. 28) will be used as a general communication channel towards the scientific community as well as the broader public. This had been started in month 1 of the project and was also used for advertising the project vacancies. Social media are also a channel to advertise network activities open to the public, e.g. conference sessions, and disseminate project related news. The coordinator is responsible for the maintenance of the accounts and updating, and all participants are encouraged to contribute by sending information or links to the coordinator. Newsletters and factsheets will address the broader public, generated by the coordinator supported by input from the participants.

4.1.4.2 Dissemination activities

Within the first reporting period, the project was introduced to the scientific community and the broader public by using the above-mentioned communication channels as the P-TRAP website and social media accounts. Although most ESRs have not started or produced relevant scientific results, P-TRAP was already presented at several conferences or scientific events. The project was presented already at the EGU2019 in Vienna to foster visibility within the scientific community, also with respect to the recruitment process. In July 2019, Andreas Voegelin (EAWAG) introduced P-TRAP by contributing a poster to the 9th international P workshop at the ETH (http://www.plantnutrition.ethz.ch/ipw9.html). In October 2019 Stefan Peiffer (UBT) represented P-TRAP on invitation at the annual cluster event with the topic “clean water”, organised by the REA. Aim of the event was to showcase the contribution to relevant scientific fields and enhances synergies among projects.

Dissemination activities for the second reporting period are planned. At the EGU 2020 a dedicated P session has been organised, with several conveners and contributions of the P-TRAP consortium. In July 2020 the UU will host a dedicated P workshop of the European Sustainability Phosphorus Platform (ESPP, see also chapter 4.1.5.2)

Table 8 shows the first dissemination activities of P-TRAP at conferences and external events, which will be intensified during the next reporting period.

Table 8: Dissemination activities of P-TRAP

Nr.	Conference name	Location	Date	Presentation [oral / poster]	Title of presentation	Authors / Conveners	Public	Link
1	EGU 2019	Vienna, Austria	7 – 12 April 2019	Poster	Diffuse phosphorus input to surface waters - new concepts in removal, recycling and management (P-TRAP)	Thilo Behrends, Sylvia Walter	yes	https://meetingorganizer.copernicus.org/EGU2019/EGU2019-13576.pdf
2	9th International Phosphorous Workshop 9	Zürich, Switzerland	8 – 12 July 2019	Poster	Diffuse phosphorus input to surface waters - new concepts in removal, recycling and management	A. Voegelin, S. Walter, T. Behrends and P-TRAP team	yes	http://www.plantnutrition.ethz.ch/ipw9.html
3	REA cluster event “Clean Water”	Girona, Spain	22 October 2019	Poster	Diffuse phosphorus input to surface waters - new concepts in removal, recycling and management	Sylvia Walter, Thilo Behrends and the P-TRAP team	no	
4	EGU2020	Vienna, Austria	3 – 9 May 2020	Conference session BG1.7	Sustainable phosphorus management and recovery: linking phosphorus and other element / material cycles	Marc Stutter, Andreas Voegelin, Sylvia Walter, Thilo Behrends, Tom Jilbert, Federica Tamburini	yes	https://meetingorganizer.copernicus.org/EGU2020/session/35258

The dissemination and exploitation activities of P-TRAP are described in more detail in the Public Engagement Strategy, submitted as deliverable D6.1. The P-TRAP Public Engagement Strategy comprise the necessary and likely key points in the communication, dissemination and exploitation of the project to ensure that institutions, companies, authorities and people with potential interest in the project are continuously informed about P-TRAP, its content, goals and consortium partners. P-TRAP aims to extend its data dissemination and exploitation beyond the project-funding period, i.e. the project's results and products are further used and marketed, the Public Engagement Strategy will be conforming the Data Management Strategy (submitted as deliverable D5.5), providing the frame conditions, and adjusted and updated over the lifetime of the project.

The dissemination and exploitation management is imbedded in the project management in Work Package (WP) 5. WP5 is led by the Project Coordinator, compulsory supported by input from all beneficiaries and non-academic partners. The dissemination and exploitation activities of all project participants will be monitored on a regular basis, and will be reported within in the consortium and towards the EU. The general rights and obligations of the consortium related to background and results are described and agreed on in the Terms and Conditions, Section 3 of the Grant Agreement as well as in Section 9 / Attachment 1 of the Consortium Agreement.

4.1.5 Impact of the Action

4.1.5.1 Impact on ESRs

The project and its network activities have first impact on the career of the ESRs: they are introduced to a highly interdisciplinary training program and get acquainted with techniques to perform first state-of-the-art measurements and developed modelling approaches. As all ESRs just recently started, no secondments have been executed in the first reporting period. Table 2 gives an overview of planned secondments, which will impact the career of the ESRs not only by increasing their professional knowledge, but also their networking and complementary skills. As mentioned above, the secondment schedule as described in the Grant Agreement needs some adjustments due to the late recruitment of several ESRs to ensure them as efficient as possible for the ESRs.

As shown in the CDPs the ESRs planned their short- and long-term career, which aims on maximising the impact of the network training.

Besides their work on their individual projects, the ESRs started to work together as a group. This is clearly visible by the self-organisation of their remote meetings, which are independent from the PIs (see chapter 4.1.3).

4.1.5.2 Impact on visibility

As described in chapter 4.1.4.2, the consortium actively disseminated P-TRAP as a project and is also searching for contacts outside the consortium. These activities will go on in the second period and intensified as soon as the ESRs can present their first scientific results. We are also fostering that ESRs will present their results and also their general project activities towards a broader public, e.g. by regular blogs. This was already planned in the proposal and had been discussed at the first annual meeting.

The presentation of the project by the website, which is an important channel towards the broader public, is lacking behind. This issue will be tackled within the next months.

In July the UU is hosting a dedicated workshop of the European Sustainability Phosphorus Platform (ESPP). This two-days workshop fits perfectly in the scheduled P-TRAP Science School: Coupling of Fe and P dynamics on global and microscopic scale, which was scheduled for month 13 in the Grant Agreement. The collaboration with the ESPP will enhance the visibility of P-TRAP as a project and enables the ESRs to enlarge their network outside the consortium.

4.1.5.3 Impact on scientific collaborations

Within the first year the P-TRAP consortium was quite active in presenting the project, although no scientific results are available yet. Scientific collaboration, fostering interdisciplinary and intersectoral exchange inside and outside the consortium will be intensified in the next reporting period as soon as first results are available.

4.1.6 Evaluation of the Action by the external Supervisory Board (SB)

The External Advisory Board (EAB) was invited to participate to the 1st Annual Meeting and was asked to evaluate the progress of the first year. Prof. Lex Bouwman (PBL/UU) and Dr. Gerwin Koopmans (WUR) represented the EAB and gave a first feedback:

> ***Introduction:***
>
> *The external advisory board found P-TRAP an interesting and inspiring project on the very important issue of phosphorus trapping and recycling in agriculture. P-TRAP is a well-balanced combination of fundamental with more applied research, with a solid organization and an enthusiastic group of PhD students and supervisors. The feedback of the external advisory board is based upon the ideas and views of Prof. dr. L. Bouwman (University of Utrecht; the Netherlands; global nutrient models) and dr. G.F. Koopmans (Wageningen University; the Netherlands; soil quality and chemistry). Unfortunately, it lacks the input of dr. M. Hupfer (IGB Leibnitz Institute for Freshwater Ecology and Inland Fisheries, Germany; biogeochemistry of lake sediments and lake management), as he was unable to participate in the annual meeting of P-TRAP. There are a few concerns and some minor recommendations/ideas for improving the work, but these need to be extended with dr. Hupfer's ideas and views, especially concerning limnological aspects of P-TRAP.*
>
> ***Concerns:***
>
> *While P-TRAPs first research objective (RO1) is to "Develop, test, and optimize novel approaches for capturing P in drainage systems and to convert the resulting P-containing Fe(III) oxides into marketable fertilizers.", the concern of the external advisory board is that the emphasis is on vivianite from many different sources and qualities (e.g. ESR2-8). Since P-TRAP intends to trap and collect phosphorus by using Fe(III) oxides in filter systems applied to pipe drains in agricultural fields, it is not clear why its value as a phosphorus-fertilizer is not tested. The latter is considered important to increase the circularity of P use within agriculture.*
>
> *The second concern is that long-term effects and impacts are not receiving attention. Such impacts include changes in soil chemical properties due to long-term application of vivianite or Fe(III) oxides loaded with P in soil P fertility field trials, the long-term effectivity of filter systems in agricultural fields and long-term impacts of remedial efforts such as addition of iron to lakes. It is clear that with a project horizon of 3 years the long-term impacts cannot be studied experimentally, but perhaps modelling can be a useful tool to study changes over prolonged periods of time.*
>
> *In general, modelling does not have a prominent role in the ESRs. It could play an important role not only for the long-term aspects, but also for extrapolation, interpreting of experimental data, and generalization of results.*
>
> ***Recommendations:***
>
> - *In view of the lack of a long-term horizon, the external advisory board recommends P-TRAP to seek possibilities to work with ongoing long-term field experiments, for example iron additions to remediate lakes suffering from a high internal phosphorus release from legacy*

phosphorus sediments. The same approach could be used for quantifying the long-term effectiveness of Fe(III) oxides in filter systems to remove P from agricultural discharge water or the possible in-situ transformation of Fe(III) oxides in agricultural soils.

- *The external advisory board stresses the importance of tuning of the work in the various ESRs to increase the output, for example by exchanging soil material and fertilizers for experiments, and using the same crops, application methods (broadcasting, band application, etc.). Although not in the workplan, the advisory board thinks that inclusion of tropical strongly weathered soils, wetland rice conditions with alternating flooding and drying conditions could be interesting topics (if time and financial means allow this extra effort).*
- *Since the potential for trapping phosphorus from water in drained fields depends on the local field and soil conditions (e.g. much less potential in heavy clays compared to porous sand), the external advisory board recommends to identify critical source areas where P-TRAPping can be successful (in drained areas). In addition, in characterizing sorption capacity of iron oxides, it is important to consider the reactive surface area of Fe(III) oxides and the initial P loading. Reactive surface area is an important factor in the binding of phosphorus by Fe(III) oxides. Furthermore, the initial P loading of Fe(III) sorbents from drinking water production plants can vary considerably, which will have an impact on the effectiveness to bind phosphorus.*
- *Assessment of the technical feasibility of remedial efforts is not a strong part of the ESRs that focus on remedial measures, for example an estimation of the quantities of by-products from drinking water production plants. This could be achieved by, for example, the use of models to estimate the long-term accumulation of phosphorus.*
- *It is important to also assess the economic feasibility of the proposed trapping and recycling of phosphorus by cost-benefit analysis, and to involve farmers and local water board authorities when assessing both technical feasibility, long-term impacts and costs and benefits.*
- *It is very important to carefully plan the secondments of the various ESRs, with due attention to those with non-academic partners (e.g. GEOTEAM, FERTIBERIA, AQUAMIN).*

The consortium will carefully review the evaluation of the EAB and implement recommendations where possible. Connecting to ongoing initiatives include e.g. the involvement of ESR3 of Deltares to long-term monitoring project, or the investigation of lakes which have been treated for a couple of years and are intensively monitored (ESR11, UU).

Cooperative efforts are already established between UBT and UU, and also EAWAG. These will be intensified during the project. We are also planning to establish a cooperation between WUR and EAWAG.

Cost benefits are currently discussed in view of a treatment experiment with Waternet, one of our partner organizations within the project.

The activities in the next reporting period will be evaluated during the next Annual Meeting and possibly further adjusted.

4.2 Outlook 2nd Reporting Period

In the next reporting period the consortium will focus on continuing the scientific work started within the first year, considering the comments and recommendations of the EAB. The consortium will intensify collaborations with related projects as well as promoting P-TRAP to the scientific community. 9 deliverables and 7 milestones are due, which planning and preparation has already started.

5. References

Wang et al.: Sulfate Local Coordination Environment in Schwertmannite, Environ. Sci. Technol., 49, 10440−104482015, 2015, doi:10.1021/acs.est.5b02660

6. History of the deliverable

Table 9: Deliverable history

Version	Author(s)	Date	Changes / Actions
1	Sylvia Walter	21 January 2020	Template of ESR report sent to ESRs and PIs
	Sylvia Walter	21 January 2020	Template WP reports sent to WP leader
	Sylvia Walter	29 February 2020	Deadline ESR contributions, WP contributions
	Sylvia Walter	11 March 2020	Requests for adjustments ESR contributions sent, except reports ESR6 and ESR11 (not received)
	Sylvia Walter	25 March 2020	First version sent to coordinator, excluding WP1 contribution (not received)
	Sylvia Walter	31 March 2020	Last WP repot received, first comments of coordinator
	Sylvia Walter	2 April 2020	Final version sent to the Executive Board and responsible PIs for input / agreement and the external Scientific Advisory Board for information (eventually input), tacit approval assumed after 8 April
	Sylvia Walter	10 April 2020	Final report, including ESR reports has been submitted.

Annex: ESR project reports

ESR1: Develop a P-TRAP system to intercept the P flux from a drained catchment area into a recreational lake

The first ESR1 resigned after a few weeks, no practical work had been done. After re-opening the position a new ESR was recruited, starting in March 2020.

P-TRAP

Diffuse phosphorus input to surface waters
- new concepts in removal, recycling and management -

D5.8 P-TRAP – 1st Progress Report

ESR 2: Effect of applying vivianite and P-containing Fe(III) oxides on P bioavailability and dynamics in different agricultural soil types

ESR	**Rochelle Joie A. Saracanlao / rj.saracanlao@kuleuven.be**
Supervisor	Erik Smolders / erik.smolders@ees.kuleuven.be
	Mieke Verbeeck / mieke.verbeeck@kuleuven.be
Co-supervisor	Stephan Kraemer / stephan/kraemer@univie.ac.at
Non-Academic secondment host	Fertiberia/Javier Brañas Lasala / jbl@fertiberia.es
Official start – end	Nov 15, 2019 – Nov 24, 2022

1. Scientific progress

1.1 Project introduction and objectives

Continuous application of P fertilizers, often more than what the crops utilize, can on the long-term exceed the natural capacity of soils to retain P. This leads to P leaching and runoff which disrupts aquatic ecosystems as a result of eutrophication. To prevent the undesirable flux of P from agricultural lands to surface waters, P can be trapped as Fe-P minerals such as vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) and P-loaded Fe(III) oxides. These products can then be reused as fertilizers thereby closing the P cycle in agricultural soils. The underlying idea is that Fe-minerals are very efficient trapping materials for binding P in groundwater (water filtration units, lake sediments) but that they can only be efficient fertiliser if Fe(III) is reduced to Fe(II), i.e. under flooded soil conditions.

The goal of this research is to determine the bioavailability of these recycled P products in lowland rice soil systems. For this work, different recycled P products have been collected from ongoing P-trapping projects, in addition to standardized materials produced in the laboratory. These P materials, mainly the Fe(II) containing P mineral vivianite and Fe(III) containing P-Fe(III) oxides will be then evaluated for their agronomic potential. As it is known that under aerobic conditions Fe-rich materials retains P very strongly, the agronomic potential of these recycled P products will be tested in anaerobic systems, namely under lowland, paddy rice growing conditions.

This research entails the following activities: 1) collection of P-loaded Fe oxides, vivianite, and possible transformation products in addition to soils varying in P and Fe responsiveness and soil properties; 2) conduct solubility and diffusion test; 3) set up long-term pot experiments to evaluate P fertilizer use efficiency of the selected P-loaded Fe oxides and vivianite relative to TSP (triple super phosphate); and 3) set up pot trials in growth chamber under controlled conditions to establish short-term agronomic efficiency of these minerals.

Various techniques will be used to understand the mechanisms underlying the plant responses to the different minerals applied in the phosphorus-poor, paddy soils. The labile P fractions will be determined by standard soil P tests but also by isotopic dilution and DGT (diffusive gradient in thin films technique). Solid phase P and Fe speciation will be measured to evaluate the transformation of the soil P and Fe pools over time after amending the soils with vivianite (collaboration with ESR 7 and 10) and with P-containing Fe-III oxides (with ESR 3 and 4). Additional research work regarding standard soil properties and soil solution characterization will be performed either in KU Leuven or during the planned secondment at UNIVIE. These experiments will be executed in collaboration with ESR 7 from EAWAG.

Standard soil properties and soil solution characterisation will be performed, either at KU Leuven or during the planned secondment at UNIVIE in collaboration with ESR 10.

Finally, an expert recommendation of the agronomic use of vivianite and P-loaded Fe oxides will be given in collaboration with Fertiberia and in cooperation with ESR 8.

1.2 Project results

1.2.1 First year

For the three months that I have been here at KU Leuven a lot of effort went into communicating with other ESRs, PIs, and non-academic partner organizations (eg. Aquaminerals, Wetsus and Fertiberia) to secure vivianite and P-loaded Fe (III) samples. I now have six vivianite samples from University of Vienna, University of Sevilla, Wetsus (3) and from the GeoInstitute of KU Leuven. One of the major experiments is that recycled P products will be made into granular / pellet fertilizers and be subsequently tested for its solubility using a continuous, sink-based extraction (Fe-bag method). A synthesized ferrihydrite will be placed in a dialysis membrane and will be used to trap P released from recycled P products. This is correlated to plant P uptake which will also be determined periodically by other P tests (e.g., DGT and Olsen) during crop experiments.

Secondly, diffusion of recycled P fertilizers from its point of application will be visualized using DGT after a given incubation time (Fig. 1). The P captured onto the DGT will then be visualized with molybdate blue, which will reflect how P diffuses. I am currently optimizing this methodology.

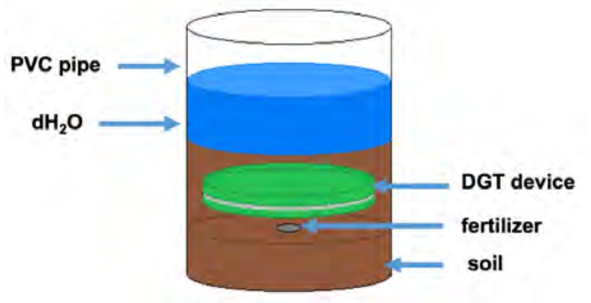

Fig. 1: Setup to visualize diffusion of vivianite and P-loaded Fe(III) oxides as fertilizers.

Lastly, crop experiments in the plant growth chamber and in the greenhouse to determine the efficiency of the different vivianite and P-loaded Fe-III oxides as fertilizers.

Soils to be used for the diffusion test and pot experiments are also being collected. To test the agronomic potential of these recycled P products, it is better to utilize soils that are anaerobic (e.g. paddy soils used for growing rice) as P is retained strongly by Fe-rich materials under oxidized conditions. We have identified poor- P soils used for growing rice in Madagascar, Tanzania (already available at KU Leuven), and Philippines based on published literature. We are also looking in Spain and Portugal through the help of Prof. Antonio Delgado.

Rice varieties that would be responsive to P fertilization were also identified. A good candidate, IR64, was suggested by Matthias Wissuwa of Japan International Research Center for Agricultural Sciences (JIRCAS).

1.3 Future plans and expected results

For the next reporting period, I should have some results already from the diffusion experiments and the solubility tests of fertilizers using the Fe-bag method. In addition, establishment pot experiments in the growth chamber as well as long-term greenhouse experiments should also commence. It must be emphasized, however, that the initiation of these research activities highly depends on the arrival of fertilizer, soil, and rice samples.

1.4 Collaborations (internal / external)

As fertilizer samples will be provided by our partner organizations Wetsus, Aquaminerals and Fertiberia, I have been in contact with them as soon I arrived in KU Leuven. I will test the vivianites and P-loaded Fe(III) oxides on their agronomic potential as fertilizers in different paddy soils. As this is a collaboration, results of the experiments will be shared to support the search for commercial applications of these materials. My secondment will also be at Fertiberia aiming on developing a recommendation of these materials for fertilizers.

Currently, I have also been in contact with Prof. Antonio Delgado from University of Sevilla, the professors and technicians from University of Philippines Los Banos, former colleagues from the International Rice Research Institute and Dr. Tovohery Rakotoson from University of Antananarivo, Madagascar regarding soil samples. Potential soil samples from Philippines, Tanzania and Madagascar were identified. Processing of regulatory permits to import them should proceed as soon as possible.

I have also been in communication with Dr. Matthias Wissuwa of Japan International Research Center for Agricultural Sciences (JIRCAS) regarding the identification of a rice genotype that is sensitive to phosphorus fertilization. The variety IR64 was suggested and just recently I have also inquired about the procurement of this variety to Ms. Flora de Guzman of the Rice Germplasm Genebank of IRRI.

1.5 Risks and difficulties

I did not encounter any issues regarding administrative matters of coming here to Belgium. Though there were minor issues (e.g. miscommunication on the exact amount of visa fees), these were easily solved. The current difficulty I have now is the availability and arrival of my fertilizer samples which dictates when will I start my experiment. It would be better if they will arrive sooner but I do understand that these fertilizers may take time to be gathered and delivered.

In addition, the procurement of soil samples and rice varieties prove to be challenging as well. As with the fertilizer samples, the rate-determining step is waiting for these items as most of them will also be imported from other countries.

2. Deliverables

ESR 2 is involved in deliverable D1.3, D1.5, D3.1, and D3.2. As all deliverables are due towards the end of the project (from months 36 to 42) no contributions were made yet.

3. Training and network activities

3.1 General training events (March 2019 – February 2020)

Event	Date (start – end)	Location (Host)	Objective / expected skills	ECTS points	Contribution	Comments
1st annual meeting	Jan 6-10, 2020	Bayreuth, Germany	How to manage Phd, work in a multicultural environment, and strategize for public engagement		Participant/ Poster Presentor	
Courses on Envi Technology and ASAC*	Nov 2019- Feb 2020	KU Leuven	Learned important principles in aquatic and soil environment	9	student	Passed the exams in these courses
Lecture on Research Integrity	Jan 16, 2020	KU Leuven	Gained responsible and ethical conduct in research		Participant	

*Applied Soil and Aquatic Chemistry

3.2 Secondments (March 2019 – February 2020)

Secondment	**Date (start – end, planned (when))**	**Location**	**Host**	**Description of work / deviations**	**Scientific / training (skills) objective**	**Results and future plans**
1	April 2020	Switzerland	EAWAG	This will be postponed this April as timing is unrealistic in terms of my current progress. Analysis will be dependent on the availability of beamtime (May 12-16, June 23-26 and later dates this year). However, EAWAG is closed to guests until April and most likely be extended due to the corona virus outbreak. I will be investigating the mechanisms underlying the transformations of P loaded Fe-oxides in soils. The plan is to prepare samples for XAS analyses, attend a beamtime, and work on data analysis. Samples can also be sent for analyses if travelling to the synchrotron will be further restricted.	Characterize Fe/P minerals throughout transformation by X-ray absorption spectroscopy.	
2	May-June 2021	Austria	UNIVIE	To measure dissolved Fe concentrations in soil solution of soils amended with vivianite.	To use nano-detection techniques for determining dissolved free Fe concentrations in soil solution	
3	Nov 2021-January 2022	Spain	FERTIBERIA	Correction is made that instead of GEOTEAM, secondment will be done in Fertiberia. Developing soil-specific recommendations on Fe/P fertilizer applications to agricultural soils based on the analysis of P and Fe bioavailability in field trials.	To formulate soil specific recommendation for the Fe-P materials.	

3.3 Conferences (March 2019 – February 2020)

No conferences have been attended during the first reporting period.

3.4 Data collected, measurement / sampling campaigns (March 2019 – February 2020)

No data have been collected as experiments are still in design phase.

4. Dissemination activities (March 2017 – February 2019)

4.1 Scientific publications

No scientific publications were done for the period March 2019 – February 2020.

4.1 Project related dissemination activities

No project related publications were done for the period March 2019 – February 2020.

ESR 3: Improving the management of surface waters draining agricultural areas to optimize the retention and recovery of Fe-associated P

ESR	Maria Victoria Barcala + Victoria.Barcalapaolillo@deltares.nl
Supervisor/ Non-Academic mentor	Leonard Osté + Leonard.Oste@deltares.nl
Co-supervisor	Thilo Behrends + T.Behrends@uu.nl
Non-Academic secondment host	Bart-Jan Vreman + BartJan.Vreman@arcadis.com
Official start – end	14/10/2019 – 13/10/2022

1. Scientific progress

1.1 Project introduction and objectives

The objective of this project is to generate knowledge to improve the surface water management in draining lowland agricultural areas with a view to retain and remove iron (Fe) associated phosphorus (P) and protect surface water from eutrophication.

Previous studies by van der Grift (2017) showed that the transport and bioavailability of P in surface waters in the Netherlands is strongly determined by the Fe present in groundwater. Fe is usually reduced in groundwater. When the groundwater extra filtrates into surface water, the Fe is oxidized. If dissolved P is present, the P will bound the Fe forming colloids and trap the dissolved P(van der Grift et al., 2018). In previous field campaigns done by van der Grift et al (2018) more than 60% of the total P concentration in surface waters in the Netherlands was particulate Fe bound P.

The speed of the process depends on temperature, pH, and oxygen availability, therefore on the season of the year. The P in the Fe-bound P particles is not readily bioavailable but can accumulate as sediment in ditches and canals.

The specific objectives of the project are:

- Create an Fe map of the shallow groundwater in the Netherlands and investigate the relationship between shallow groundwater quality and surface water quality at a national level. For this available national information from DINO (Dutch acronym for Data and Information of the Dutch Subsurface) and LMG (Dutch acronym for National Groundwater Quality Monitoring Network) will be used and information from the database "*water plants and water quality*" in collaboration with Nijmegen University. This database collects information about surface water quality and sediment over 700 points in the Netherlands, half of them measured during two seasons (summer and winter), the other half during one season. The information generated can be used to calculate the load of P and Fe transported in surface waters and to detect where Fe-bound P transport is higher in the Netherlands.
- Understand how the Fe-bound P particles are transported. Sediment transport will be studied at two different scales. For the large scale, river sediments will be sampled and for the smaller scale high frequency monitoring of a one-farm ditch will be investigated. Lab work will accompany fieldwork for better understanding of the processes. The secondment at KUL will serve for this research question. They have an experimental set-up (flume) where different P/Fe ratios, dissolved oxygen concentration and temperature can be modified and the influence on the sediment transport

can be assessed. The information generated can be used for example to predict were rich P sediments will accumulate in a river and to improve the design of retention basins for P particles.

- Evaluation of P-TRAP measures. Measures for P retention in lowland surface water catchments are often implemented but their effectiveness is not evaluated in the long term in the Netherlands. This information can be used to improve P-TRAP management. Together with projects inside Deltares and ARCADIS, P trap measures will be assessed. Many different techniques, as for example retention basins and iron coated sand filters, have been implemented but there is little information about their effectiveness on the long run. The secondment at ARCADIS will serve for this research question ARCADIS has been involved in several applied projects related to P retention. Variables related to farm measures in the Netherlands can be evaluated as: P removal efficiency, cost, feasibility of P recovery, farmers acceptance of the measure. Also, different measures can be related to different areas of the Netherlands identified in the first point with the Map.

1.2 Project results

1.2.1 First year

ESR 3, Victoria Barcala, was appointed in May 2019 after a recruitment procedure. She moved to the Netherlands in October and started working on the 14-10-2019. So far, ESR 3 is involved in different Deltares projects related to P-Trap, where she can collaborate and also gain valuable information relevant for the set research questions. ESR 3 had meetings with the partners of the projects where she is doing the secondments and discussed the objectives for the planned activities. ESR 3 attended the first P-TRAP annual meeting in Bayreuth, with the whole P-TRAP consortium.

ESR 3 is formally enrolled in the Ph.D. program at the Geoscience Faculty of Utrecht University and is also a guest employee. ERS 3 had a first contact with her promotor, Jack Middleburg and has periodic meetings with her supervisor at Deltares and Utrecht University. ESR 3 attended Utrecht University Seminars and did a presentation on her research. As a formal task the CDP has been achieved.

ESR 3 is working on building a Fe map, of shallow groundwater of the Netherlands and the correlation between Fe in groundwater and other ions (SO_4, NO_3, Ca, Mg, Al, PO_4) and other available data as: geology, soil type, land use, groundwater levels. To obtain these correlations machine learning techniques are being used. The correlation coefficients between these parameters and the Fe concentration in ground water is 0.75 using the whole database and the Random Forest Algorithm. The trend in the Fe concentration in groundwater given certain characteristics can be predicted. The map obtained so far is not continuous, it only has discrete data points. There are 62578 points from 0 to 30 m depth and 6871 points from 0 to 5 m depth. From these points we have the Fe information, the open source data, but information about the other ions is sometimes missing. No clear geographical regions with higher Fe were detected, high Fe values are scattered all over the country. Nevertheless, some trends can be detected, as higher values as depth increases, higher values in agricultural land use than natural land use.

ESR 3 visited two field sites she is going to use on the research. Both sites are in drained agricultural fields. One site is the tulip area, this area has low Fe concentrations in groundwater and therefore the dissolved P is one of the highest in the country, here iron coated sand filters were implemented as a mitigation measure in some fields. Nevertheless, the P removal is not working as expected, one of the objectives in this field site is to understand why. The other site is a cattle farm, there is data from continuous monitoring of nutrients over the past year, mitigation measures will be implemented soon, so a detailed evaluation of the effect of the measures can be done. On this last farm samples were taken to analyze special changes in PO4 and Fe concentration in the ditches.

1.3 Future plans and expected results

For the next year ESR 3 expects to have finished the Fe Map of shallow ground waters in the Netherlands and have gained a better insight of the influence of Fe in ground water on the formation of Fe bound P particles. On the 26th of March there is a meeting planned with Nijmegen University to use their data base from the "water plant and water quality" project. Possibly, this study will be complemented with satellite images of the canals where the Fe-bound P particles can be seen.

Also, ESR 3 expects to have a detailed plan of the field work and lab work activities and to have done the secondment at Utrecht University to learn about sequential extraction and other laboratory techniques as XRF and IC. For the sequential extractions' sediments from the ditch of the cattle farm will be used. ESR 7 will come to Deltares for his secondment and ESR 3 join will join field work activities, collecting rich Fe-P particles.

Another objective for the year is to write a scientific paper in collaboration with Joachim Rozemeijer (Deltares) about the P behaviour on the high frequency monitored farm with the available data and do lab work to answer the questions that arise. For this ESR 3 will take once a week a course on scientific writing at Utrecht University during 9 weeks.

1.4 Collaborations (internal / external)

I) Collaboration with four other internal projects from Deltares:

- *Verbeteren emissieberekeningen zware metalen voor de Emissie Registratie (*Improving emission calculations for heavy metals for Emission Registration*)*
- *Grip op Slib (*Grip on Sediments*)*
- *Fosfaatroutes (*Phosphate Routes*)*
- *Waterplanten en waterkwalitei (*Water Plants and Water Quality*)*.

These collaborations will continue next year. The projects are directly related to the research objectives. The collaboration includes participation on fieldwork, knowledge exchange, and shearing data.

II) Collaboration with Utrecht University: enrollment, attendance to the geochemistry faculty seminars, attendance periodic meetings with other ESRs, planed a formal meeting with mt promotor for the next year, plan lab training together with ESRs placed at the university (ESR 6 and ESR 11).

III) Collaboration with ESR 7: for next year, look for field work sites and probably take samples and complement lab work for his secondment at Deltares.

IV) Contact established with Uruguayan researchers working on phosphorus to collaborate, namely Lucia Boccardi, Hector Garcia, and Diana Miguez.

1.5 Risks and difficulties

No specific difficulties were detected. Nevertheless, the type of work, particularly the field work, always require cooperation with the land owner (farmer), particularly regarding agricultural management and measures to reduce phosphorous transport to (larger) surface waters. This requires careful communication and flexibility in planning, so we will regularly check the planning.

2. Deliverables

- D.1.3 Guidelines and recommendations for retaining and recovering Fe-bound P in drainage systems (Deltares PU, Month 36)
- D3.1 Kinetic models for the transformation of P containing Fe phases (EWAG CO, Month 36)

- D3.2 Report on the fate of P during Fe phase transformations (UNIVIE 40)

The deliverables are due towards the end of the project, nevertheless, the career development plan written tries to set activities needed to write “Guidelines and recommendations for retaining and recovering Fe-bound P in drainage systems”. Research question number 1 and 3 together evaluate different cases and the best technologies to use on each case. Research question 2 can provide useful information about how to design retention basins or to set maximum velocities on pumping stations or where to build a weir to accumulate sediments. All this can be included in the deliverable document.

The joint field and lab work planed with ESR 7 will make contributions to the deliverable D3.1 “Kinetic models for the transformation of P containing Fe phases”.

3. Training and network activities

3.1 General training events (March 2019 – February 2020)

Event	**Date (start – end)**	**Location (Host)**	**Objective / expected skills**	**ECTS points**	**Contribution**	**Comments**
P-TRAP workshop	6-1-2020 to 8-1-2020	UBT Bayreuth Germany	Soft skills: communications, time management, networking		Participation + pitch +poster	
Language course (Dutch)	5-2-2020	Babel Institute, Utrecht	A1 -A2 Dutch Language course, 15 personal lessons			
Online Big data course	12-2019	University of Waikato, New Zeeland	Online course on big data and regression techniques in machine learning		online course	No certificate was given because of the dates it was taken

3.2 Secondments (March 2019 – February 2020)

Secondment	**Date (start – end, planned (when))**	**Location**	**Host**	**Description of work / deviations**	**Scientific / training (skills) objective**	**Results and future plans**
ESAS*	April-May 2020	The Netherlands	UU	ESR 6 will transfer knowledge acquired at UU to ESR 3 and 9 on sequential extraction of P. Knowledge transfer of Fe and S sequential extraction techniques will be done by other UU PhD’s students.	Learn laboratory techniques that will be used further during the research, for example sequential extractions of P, Fe and S.	In the future these techniques will be used to analyse the mineral content of the sediment in the cattle farm in Hupsel.

* exchange of scientific methods, approaches, or skills

No secondments were done during the period March 2019 – February 2020. The secondment at Utrecht University is planned for April-May 2020. The objective of the secondments is to learn laboratory techniques that will be used further during the research, for example sequential extractions.

The secondment at KUL is planned for 2021 and in Arcadis for 2022.

3.3 Conferences (March 2019 – February 2020)

No conferences were planned for the period March 2019 – February 2020.

3.4 Data collected, measurement / sampling campaigns (March 2019 – February 2020)

Data	Date (start – end, planned (when))	Location	Description of work	Scientific objective	Samples (nature / number)	Results and future plans
LMG Database & DINO Database	11-2019	Deltares	Database of groundwater quality from 1900 to 2017 of . (DINO and LMG)	Better understanding of the characteristics of the water extra filtrating to surface water in the Netherlands	Number of samples over 90.000	Iron map and relation between groundwater and surface water quality
Info on sampling sites for milestone 8	1-2020	Deltares	Descriptive information about sampling sites	Selection of interesting sampling sites		Write deliverable and select sampling places
Digital Geographic information of the NL	11-2019 to 1-2020	NHI and Deltares	Geographic information of the Netherlands	Better understanding of the characteristics of the water extra filtrating to surface water is the Netherlands	Different geographic information as raster for soil type, land use, geology, groundwater level. Public date available on https://data.nhi.nu/	Iron map and relation between groundwater and surface water quality
Fieldwork on two sites	21-2-2020	Huppel and Harlem	Field work: water and sediment sampling	Plan the field work for the project. Have quantitative data of the selected sampling places	PO4, total Fe, NO3, sediment samples	Results will be ready on the week of 9/3/2020

4. Dissemination activities (March 2017 – February 2019)

4.1 Scientific publications

No publications were planned for the period March 2019 – February 2020.

4.1 Project related dissemination activities

Dissemination activity	Date	Location	Type of audience	Size of audience
2 Blog posts about the P-TRAP annual meeting and a personal blog introducing ESR3	1-2020	P-TRAP webpage (Public)	scientific, industry, civil society, general public, policy makers, media, investors, customers (could be any)	unknown
Dissemination activities included P-TRAP annual meeting in Bayreuth where poster and pitch were used to communicate the research.	1-2020	Bayreuth, Germany	P-TRAP consortium	20 to 30 people
Presentation of the research to the Geoscience group of Utrecht University at one seminar and at one internal meeting at Deltares.	11-2019	Utrecht, the Netherlands	Scientific community	20 to 30 people

References

Van der Grift, B. (2017): Geochemical and hydrodynamic phosphorus retention mechanisms in lowland catchments (Thesis)

Van der Grift, B., Osté, L., Schot, P., Kratz, A., van Popta, E., Wassen, M., Griffioen, J. (2018): Forms of phosphorus in suspended particulate matter in agriculture-dominated lowland catchments: iron as phosphorus carrier, Science of the Total Environment, 631-632, 115-129, https://doi.org/10.1016/j.scitotenv.2018.02.266

ESR4: Converting Fe residual materials into filter-stable sorbent materials for P removal

ESR	Oleksandr Bolielyi, o.bolielyi@geosfreiberg.de
Supervisor	Susan Reichel, s.reichel@geosfreiberg.de
Co-supervisor	Stefan Peiffer, s.peiffer@uni-bayreuth.de
Non-Academic secondment host	AQUAMIN,Olaf van der Kolk, vanderkolk@aquaminerals.com
Official start – end	01.12.2019 – 31.11.2022

1. Scientific progress

1.1 Project introduction and objectives

The ESR's 4 project is aimed at the study of adsorption of phosphorus (P) at the iron-based sorbent, called schwertmannite. Schwertmannite is produced from the mine drainage. This drainage contains high concentration of ferrous iron (Fe (II)). During conventional treatment the water is aerated and lime milk is added to adjust the pH, oxidize the ferrous iron and separate the ferric hydroxide sludge. An alternative technology designed by G.E.O.S. uses the naturally occurring microbial iron oxidation to produce and precipitate schwertmannite. Nowadays, there is a pilot plant located in Tzschelln near opencast mine in Nochten. It produces 10-15 tons of schwertmannite per year. This schwertmannite will be analysed and converted to adsorbent filter-stable material and compared to modern commercial adsorbents towards P removal.

Since the schwertmannite is a quite fine material, the real challenge is to create filter-stable agglomerate, which can be used in the filter cartridges for P removal from water. In order to develop stable agglomerates ESR 4 will apply existing agglomeration techniques or develop new ones. If the filter-stable filter material will be obtained, then via field tests it can be evaluated, whether developed filters are worth using. In case the created filter-stable adsorbents are not suitable, existing materials from GEOS can also be used for the field tests.

1.2 Project results

1.2.1 First year

ESR 4 was hired and started working on 1st December of 2019. Since then ESR 4 got to know with state of the art and research, ESR 4 have been looking through various reports from projects made in GEOS as well as some basic literature on iron compounds and their oxidation, adsorption processes. In reference to recent reports it was decided to study the raw material properties first: moisture content, adsorption capacity and kinetical parameters of raw schwertmannite such as contact time, pH, temperature, influence of phosphorus initial concentration.

Table 1: Required information of physical characteristics of materials in P-TRAP systems

Characteristics	Method
Dry mass [%]	
Particle size [mm]	DIN EN ISO 17892-4:2017
Bulk density [kg/dm^3]	DIN EN 1097-3:1998
Particle density [kg/dm^3]	DIN EN 1097-6:2013
Oversize, Undersize % by mass	DIN EN 933-10
Porosity %	-
Specific surface [m^2/g][1]	DIN ISO 9277:2014
Pore size (average) [nm][1,2]	DIN ISO 15901-1:2019-03

[1] washing and drying of the material prior to measurement

[2] if necessary, depending on type of material

We have started to work on our own methods for studying raw material schwertmannite properties during batch experiments. As there is no existing guideline or guidance document for assessing adsorption capacity of granular materials a test method which was elaborated by Technical University Dresden in past adsorption studies (Richter 2016) and adjusted based on published methodologies (Dou et al. 2013, Ye et al. 2015) can be applied (see milestone MS7 report). However, schwertmannite is a specific iron-based adsorbent, so some parameters might change, such as rotation speed or incubation time. All the experiments yet were carried out with model solution. It was prepared from $Na_2HPO_4*H_2O$ with a concentration of ortho-P 100 mg/L. The batch experiment was carried out without pH adjustment. Initial pH of solution is 8.6. pH after finishing batch experiment was 7.68. The raw material, which was used is aged schwertmannite (schwertmannite sample from pilot plant, dried at 50°C and stored for several months). Approximate concentration of schwertmannite used is 200 mg/l for dried material. Bath experiment was carried out for 24 hours. After 24 hours samples were taken and residual concentrations of phosphates were defined photometrically. The phosphate spectroquant test (Merck) was used.

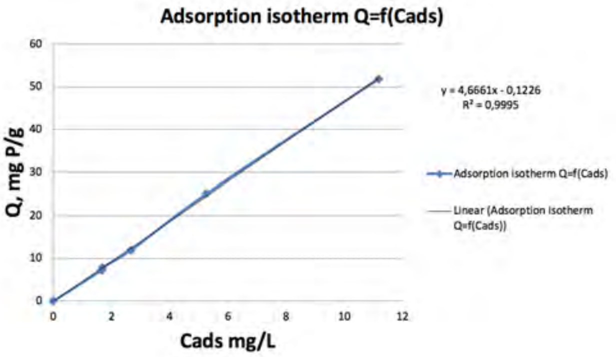

Fig. 1: Batch experiment adsorption isotherm

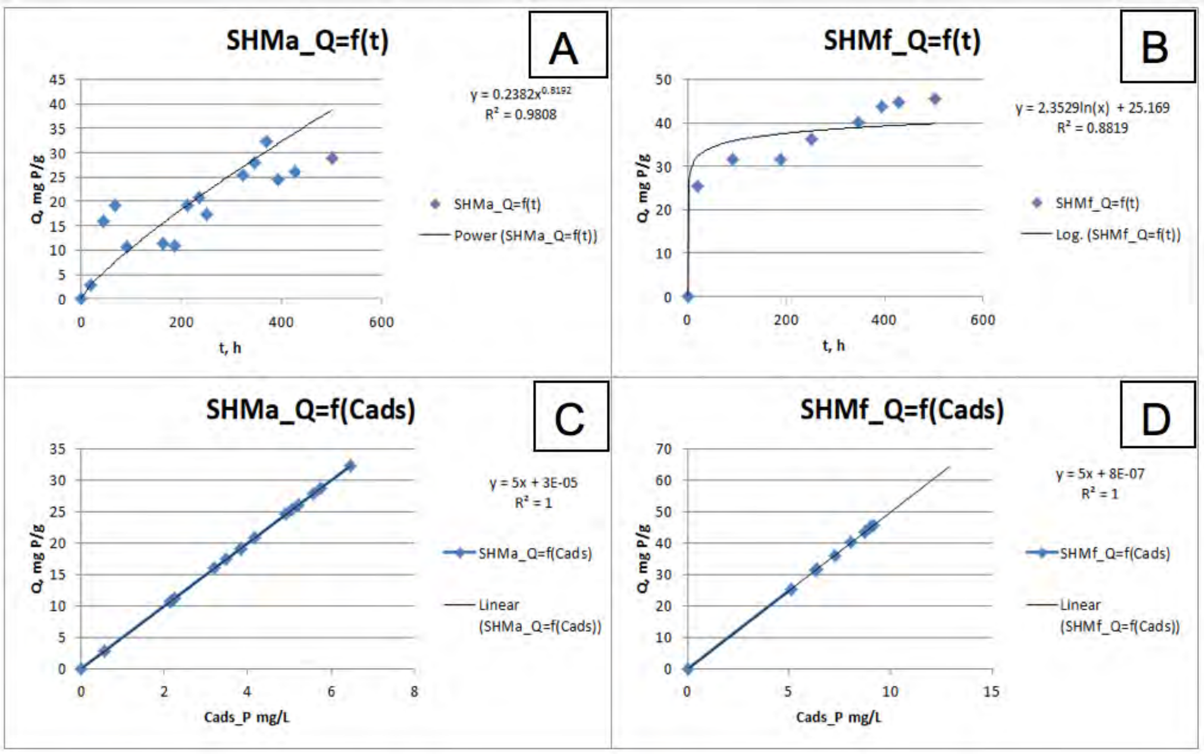

Fig. 2: Kinetical data of P adsorption at Schwertmannite: at the aged schwertmannite (A); at fresh schwertmannite (B). Adsorption isothertms: at the aged schwertmannite (C); at fresh schwertmannite. (D).

The batch experiment showed that maximum adsorption capacity cannot be reached during 1 day (see further results of kinetics experiment). Conclusion: Unclear. Adsorption isotherm exhibits linear trend. That would mean schwertmannite has enormous amount of active sites, which cannot be filled with phosphates within 24 h in neutral media.

Kinetic experiments yet were carried out for more than 500 hours. Model solution prepared from $Na_2HPO_4*H_2O$ with concentration of ortho-P 100 mg/L was used. pH was adjusted to 7.5 using 0.1 M HCl. The raw materials, which were used, are the aged schwertmannite and fresh schwertmannite collected from pilot plant in Tzschelln on 11th of December (Fig. 2). Fresh wet material was dried at 50°C. Approximate concentration of Schwertmannite used is 200 mg/l for dried material. Samples were placed into 500 ml bottles and were shaking constantly at 150 rpm. Samples were analysed every 24 hours photometrically with the use of phosphate spectroquant tests (Merck, molybdenum blue method).

Results confirmed, that fresh raw material has higher adsorption capacity then the aged one. Schwertmannite can remove up to 46 mg P per g of fresh schwertmannite (1.5 mmol P/g), while aged can remove up to 29 mg P/g (1 mmol P/g). Maximum of adsorption capacity is not reached within 500 hours with concentration of 100 mg P/L. During kinetic experiments pH slightly declined up to 7.2.

Further researches will be carried out with other raw materials, like iron sludges. We assume that mixture of Schwertmannite with other raw materials may lead to better agglomeration characteristics obtained. There is an option to carry out experiments in acidic and alkaline media.

(also see WP1 1st progress report)

1.3 Future plans and expected results

Since the raw material studies are in progress it would be wise to continue the research of the raw material schwertmannite properties and start looking for suitable agglomeration techniques to create a filter-stable adsorbent. The properties of the created adsorbent can be studied in the same way, as the raw material was (see milestone MS7 report). We also consider starting research of P removal from the samples of waters from sites (e. g. field site near Bayreuth, Germany).

1.4 Collaborations (internal / external)

With ESR 9 we have discussed the Schwertmannite behaviour inside solutions, which contain phosphorus. That helped us to understand more about the possible mechanism of P adsorption at Schwertmannite surface. We have exchanged materials from batch and kinetics experiments, so we could confirm that the data and techniques applied are reproducible. We are looking forward to exchange more knowledge and upcoming results.

For the next reporting year, it is planned to take secondment at UBT in July/August 2020 in order to study techniques for surface analysis of the materials (raw, agglomerated and loaded). Another secondment will be carried out with Aquaminerals from mid-September to mid-December. There ESR 4 is going to gain knowledge in agglomeration techniques, required parameters, which should be met in order to produce filter-stable adsorbent.

1.5 Risks and difficulties

No difficulties were encountered so far.

2. Deliverables (full text)

ESR 4 is involved in the deliverables D1.1, D1.2, D1.3. Nothing has been published yet. Data collection and evaluation are in progress.

3. Training and network activities

3.1 General training events (March 2019 – February 2020)

Event	Date (start – end)	Location (Host)	Objective / expected skills	ECTS points	Contribution	Comments
TSCS 1 & 1st annual meeting	06.01.2020 – 10.01.2020	Bayreuth University	Meeting with all members of consortium. Attending workshops on effective management of scientific work, intercultural cooperation. Brief introduction to P-TRAP for ESRs and progress overview. CDP discussion and future researches and organization planning.		Participating, presenting poster, short pitch.	

3.2 Secondments (March 2019 – February 2020)

Secondment	Date (start – end, planned (when))	Location	Host	Description of work / deviations	Scientific / training (skills) objective	Results and future plans
UBT	20.07.2020-20.08.2020	Bayreuth	University Bayreuth	The study on the surface of the adsorbents requires application of specific conventional and innovative techniques.	Training on techniques for surface analysis of the materials (raw, agglomerated and loaded)	After trainings are complete ESR 4 can can apply techniques (FTIR, XRD, Mossbauer spectroscopy etc.) to define the efficiency of different adsorbents towards Phosphorus removal.
Aquaminerals	21.09.2020-21.12.2020	Utrecht	Aquaminerals	Since agglomeration of raw materials into adsorbents is the most important and challenging task of the ESR 4, gaining knowledge in agglomeration techniques and adsorbent's requirements for agglomeration is essential.	Trainings on agglomeration techniques and adsorbent requirements for filters.	By getting knowledge in agglomeration techniques it will then be possible t decide which technique is the best for production of agglomerated filter-stable adsorbents.

Be aware, that secondment which was planned in month 10-11 in UU was replaced with secondment at UBT in months 17-18 due to logistic and direct coherence/correlation between the scientific and practical approaches we use.

3.3 Conferences (March 2019 – February 2020)

No conferences have been attended in this reporting period.

3.4 Data collected, measurement / sampling campaigns (March 2019 – February 2020)

Data	Date (start – end, planned (when))	Location	Description of work	Scientific objective	Samples (nature / number)	Results and future plans
SHM sorption isotherms	28.01.2020 – 05.02.2020	GEOS	Conduct test batch experiments to create standard methods for adsorbents properties evaluation	Come up with standard procedure for comparison of different adsorbents towards P removal	5 samples	Results were obtained for aged Schwertmannite. Method development is in progress. Planning to apply the method with fresh sample
SHM Kinetical data	11.02.2020 – 29.02.2020	GEOS	Kinetic tests	Study and comparison of Schwertmannite (aged and fresh) raw material in model solution of P	6 samples (2 samples with 2 parallels)	Observations on kinetic behaviour and properties of P adsorption at Shwertmannite.

4. Dissemination activities (March 2017 – February 2019)

4.1 Scientific publications

No scientific publications were done for the period March 2019 – February 2020.

4.1 Project related dissemination activities

No project related publications were done for the period March 2019 – February 2020.

References

Dou, X., Mohan, D., Jr Pittmann, CU (2013) Arsenate adsorption on three types of granular schwertmannite. Water Research, vol. 47, p. 2938-2948.

Richter, J. (2016) Pilotmaßstäbliche Eignungsprüfung von Schwertmannit-Adsorbenzien zur Behandlung von Sickerwässern einer ehemaligen industriellen Absetzanlage der Uranerz-Aufbereitung, Master Thesis, Technical University Dresden

Ye, J., Cong, X., Zhang, P., Hoffmann, E., Zeng, G., Wu, Y, Zhang, H., Fan, W. (2015) Phosphate adsorption onto granular-acid-activated-neutralized red mud: parameter optimization, kinetics, isotherms, and mechanism analysis, Water Air Soil Pollut, p. 226-306

D5.8 P-TRAP – 1st Progress Report

ESR 5: Microbial technologies for converting P- loaded Fe (III) oxides

ESR	Lordina Ekua Eshun; lordina.eshun@manchester.ac.uk
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Co-supervisor	Prof. Dr.Antonio Delgado; adelgado@us.es
Non-Academic secondment host	Fertiberia
Official start – end	01/2020 – 01/2023

1. Scientific progress

1.1 Project introduction and objectives

Within the context of P-TRAP, ESR 5 focuses on the development of novel biotechnological route for the conversion of phosphorus–loaded Fe(III) oxides. Thus, microbial based processes would be utilised to convert P-loaded Fe(III) oxides into the bioavailable Fe(II) phosphate mineral vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$). This phosphate rich mineral will then be assessed for its ability to be used as a soil conditioner (fertilizer).

Fe(III) minerals such as ferrihydrite are naturally abundant in the environment such as in sediments/soils, waste materials, wastewater etc. Therefore, using ferrihydrite will serve as an appropriate raw material (starting material) for the production of Fe(II)-bearing minerals (e.g. vivianite) by Fe(III)-reducing bacteria (*Geobacter sulfurreducens*, *Shewanella oneidensis)* in the presence of phosphate. Subsequent experiments will make use of other waste materials and indigenous microbial inocula. This way, the cost of starting materials can be reduced.

The pathways of bioconversion from ferrihydrite to bio-vivianite by Fe(III)-reducing bacteria would be optimised to understand the sorption mechanisms of phosphorus onto Fe(III), and its impact of the end-point Fe(II)-bearing mineral. This will be done together with ESR 4. The fertilizing ability of the produced bio-vivianite will be investigated together with ESR 6, 7 and 8 and through collaboration with FERTIBERIA, a non-academic partner organisation (NAPO) involved with P-TRAP.

1.2 Project results

1.2.1 First year

My contract started on 20th January 2020 but I officially started on 27th due to a delay in obtaining my Biometric Residence Permit (BRP).

Experiments concerning my projects have not been started yet but I hope to start by 1st week of March. In the meantime, I´m focusing on preparing a comprehensive literature review of the area, and also completing training and risk assessments to underpin my initial experiments.

1.3 Future plans and expected results

The scientific and training plan for the next reporting period are focused on the development of research skills such as performing laboratory experiments with Fe(III) reducing microorganisms, developing new expertise that will be useful for ESR 5 project. Some of such experiments include the following:

1. Bioreduction experiments

- Growth of *Geobacter sulfurreducens* in NBAF media

- Use of soluble Fe(III) to produce vivianite through reduction by Fe(III) reducing bacteria in the presence of phosphate
- Synthesis of Ferrihydrite (insoluble Fe(III) oxide)
- Bioreduction of Ferrihydrite by Fe(III) reducing bacterium in the presence of phosphate
- Effect of mediators (electron shuttles) (AQDS, Riboflavin, etc..) on the reduction of Fe(III) to Fe(II) and their respective effect on vivianite formation
- Which conditions/parameters (pH, temperature, electron donor, molar ratio of P/Fe, …) can be steered for vivianite formation
- How does phosphate affect the biotransformation of Fe(III) by Fe(III) reducing bacteria

2. Characterization of the bio-reduced products (Fe-P solids): Techniques such as Omic techniques, synchrotron based X-ray spectroscopy, beam time, advanced biomineral analysis. The use of these techniques for characterization experiments is geared towards acquiring new skills as well as reporting towards WP 3.

3. P-TRAP Training module (Science school/Transferable skills Training course 2 in July 2020 at Utrecht)

1.4 Collaborations (internal / external)

No collaboration has been done for this reporting period.

For the next reporting period, it is scheduled to perform an experiment on Fe Chlorosis at the University of Seville (US) during September 2020. This experiment will be performed with ESR 8, hence communications regarding the quantities of biovivianite needed for the pot experiments are already underway.

It is also planned that the Chlorosis experiment at US be combined with the Secondment at FERTIBERIA. This is yet to be finalised.

1.5 Risks and difficulties

Although the official start date for ESR's was September 2019, I had to start on the 20th of January 2020. This is due to delays caused by government regulations concerning the advertisement of the project ESR 5. This resulted in a delay in the visa application thereby making it impossible for me to arrive at the University early.

2. Deliverables

ESR 5 is involved in the deliverables D1.4, D1.5, D3.1. Due to the start date, no contributions have been done.

3. Training and network activities

3.1 General training events (March 2019 – February 2020)

Event	Date (start – end)	Location (Host)	Objective / expected skills	ECTS points	Contribution	Comments
Critical Reading:	18/02/2020	University of Manchester	This workshop explores how to review literature critically and effectively and looks at		Just participating in this workshop	I learnt that; Being more critical about papers you read means you not only reading for

Techniques and Strategies (FEPSS 8033)	(10:00am – 12:00pm)		various techniques that can be used to obtain an optimal amount of information from written material in a time-efficient manner.			information sake but you also reading to question their approaches/methodology to see if their results/conclusions can be trusted.

3.2 Secondments (March 2019 – February 2020)

Secondment	Date (start – end, planned (when))	Location	Host	Description of work / deviations	Scientific / training (skills) objective	Results and future plans
ESAS*	September – October 2020	Spain	US	At University of Sevilla, Fe(II) minerals that has been produced through reduction by Fe(III) reducing bacteria will be tested on Fe depleted soils/sediments. We aim to investigate whether the biogenic Fe(II) mineral can be used in soils affected with Fe Chlorosis and if Fe is bioavailable for use by plants.	Application of Fe containing minerals to Fe depleted soils/sediments to prevent Fe chlorosis	

* exchange of scientific methods, approaches, or skills

3.3 Conferences (March 2019 – February 2020)

I was not able to attend the conference in Germany due to delays associated with obtaining my UK Visa.

3.4 Data collected, measurement / sampling campaigns (March 2019 – February 2020)

No data have been collected yet

4. Dissemination activities (March 2017 – February 2019)

4.1 Scientific publications

No scientific publications were done for the period March 2019 – February 2020.

4.1 Project related dissemination activities

No project related publications were done for the period March 2019 – February 2020.

D5.8 P-TRAP – 1st Progress Report

ESR 6: Process controlling P dynamics upon reductive transformation of P containing Fe minerals

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Non-Academic secondment host	AquaMinerals, Olaf van der Kolk, vanderkolk@aquaminerals.com
Official start – end	01/12/2019 - 30/11/2023

1. Scientific progress

1.1 Project introduction and objectives

Reductive dissolution of iron (hydr)oxides by dissolved sulphide is important in regulating the cycling and mobility of phosphate in aquatic systems. ESR6 of P-TRAP will mainly focus on the kinetics and mechanism of reductive transformation of P containing Fe(III) oxides and the consequences for P release in laboratory experiments. This part of the project will also contribute to studying the fate of phosphate during the reductive transformation of iron minerals in bioreactors. The goal is to develop deterministic models for describing and predicting the phosphate dynamics during the reduction or recrystallisation of phosphate-containing iron minerals. The results will be used to characterise and constrain the prerequisites for long-term binding of phosphate in lake sediments.

1.2 Project results

1.2.1 First year

ESR6 aims at determining the mechanisms and kinetics of phosphate release during the sulfidation of Fe(III)-(oxy)(hydr)oxides (Fe-oxides). The reaction of sulfide with Fe-oxides is considered a relevant pathway for the mobilization of solid-bound Fe and P in sediments. To investigate the kinetics of Fe oxide sulfidation, we use mixed flow-through reactors (Fig. 1), which allow measuring reaction rates at controlled steady-state conditions.

I have started to design and perform experiments to determine the release of P upon the reaction of Fe oxides, which are initially binding P, with sulphide.

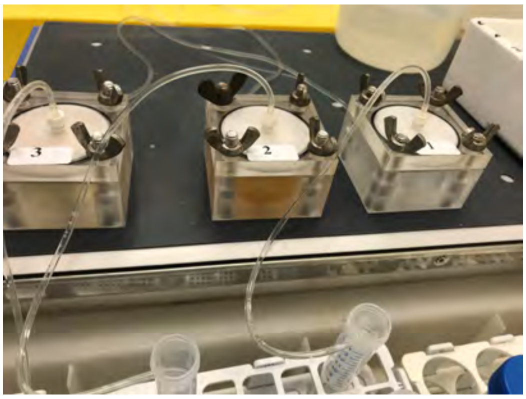

Fig. 1: Flow-through reactor setup. The picture shows the flow-through reactors which are installed on a stirrer plate to keep the suspension well mixed throughout the experiment. Solutions are pumped through the reactor at controlled flow rates using a peristaltic pump. The reactor contains a magnetic stir bar. The solids are retained in the reactors by membrane filters which is installed before the outlet opening at the top.

As an experimental approach, it was decided to use flow-through reactors, which allow determining the progress of the reaction at controlled conditions. The experimental set-up has been developed and first tests have been performed, including breakthrough curves using inert electrolyte solutions and first experiments with iron oxides in the reactor and sulphide in the inflow solutions. The analytical procedures for determining dissolved sulphide, Fe and P in the out flow have been tested. For the first experiments, lepidocrocite (γ-FeOOH) was used, which forms in natural environments upon the oxidation of Fe^{2+} containing solutions. Adsorption of P to lepidocrocite has been investigated and first reactor experiments with lepidocrocite containing adsorbed P are currently being performed.

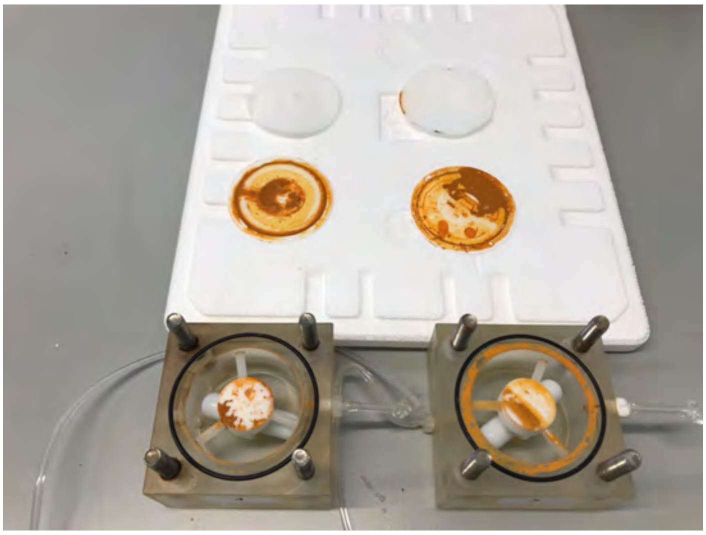

Fig. 2: Testing the recovery of reacted solids at the end of the experiment. The majority of the solids could be recovered from the membrane filters, but a part was sticking behind the holder of the magnetic stir bar. For this reason, another type of magnetic stir bar was tested which does not need a holder.

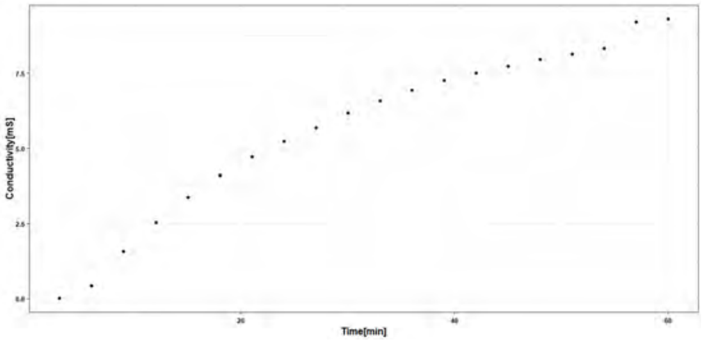

Fig. 3: Breakthrough curve of 0.1 M NaCl through the flow-through reactor.

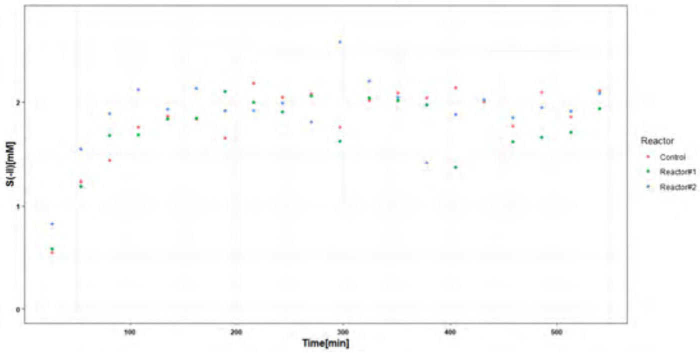

Fig. 4: Time evolution of sulfide concentrations in the outflow of the reactors during the lepidocrocite sulphidisation experiment. The control reactor does not contain Fe oxide.

Additionally, methods for characterizing Fe containing solids are currently being tested. This includes Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray diffraction (XRD), and electron microscopy. The experimental system which has been set up consists of multiple flow-through reactors (Fig. 1). The system has been tested for leakage, flow rates were calibrated, and test runs were performed with inert electrolytes. Protocols have been developed for preparing anoxic, sulfide containing solutions, and for designing a sampling scheme. The analytical procedures for measuring dissolved iron, phosphate and sulfide in the outflow of the reactors have been tested.

Furthermore, a procedure has been tested to recover the solids at the end of the experiment under anoxic conditions for detailed characterization. The method is based on pumping N_2 gas through the flipped over reactor. The idea is to collect the solids on the membrane filter (Fig. 2). The Fe-oxide lepidocrocite (γ-FeOOH) has been chosen for our first experiments. Suspensions containing lepidocrocite with and without adsorbed phosphate have been prepared. For testing the experimental design, the reactors were filled with deionized water and the breakthrough curve of a 0.1 M NaCl solution has been measured by monitoring the electric conductivity in the outflow (Fig. 3). The shape of the break-through curve can be compared to the theoretical curve based on the flow rate, the volume of the reactor, and the assumption that the reactor is well-mixed. The test demonstrated that the reactors behaved as well-mixed reactors.

First experiments with lepidocrocite and sulfide have been performed at pH 8.3. The pH has been selected based on preliminary experiments and will be varied systematically in subsequent experiments. The pH is maintained by a buffer added to the sulfide solution. pH measurements in the outflow indicate that pH changed by less than 0.3 units. Throughout the experiments, aliquots of the outflow were collected for determining the concentrations of phosphate, iron and sulfide. Results show that the concentration of sulfide in the outflow increased at the beginning of the experiment and then reached a steady-state (Fig. 4).

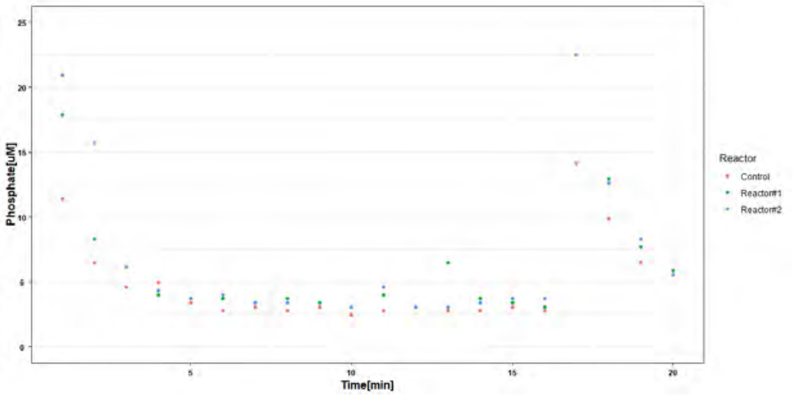

Fig. 5: Time evolution of effluent phosphate concentrations in sulfidation experiments with phosphate-sorbed lepidocrocite. The control reactor does not contain Fe-oxide.

However, relatively large variations (>10%) in the effluent sulfide concentrations were observed over time, which currently impede the precise determination of sulfide consumption rates. We are therefore working on improving the robustness of the sulfide determination. Also, other measures are currently being tested to improve the quality and significance of the results, such as adjusting the flow rates.

In first experiments with Fe-oxides with adsorbed phosphate, a pulse of increased phosphate concentration was observed when sulfide started to enter the reactors (Figure 5). However, not all adsorbed phosphate became released. That is, phosphate release continued at a constant pace after the initial pulse. Resuming the pumping after an interruption of several hours resulted in a significant increase in phosphate concentrations in the outflow. This supports the conclusion that the release of phosphate due to Fe-oxide sulfidation is controlled by reaction kinetics and occurs on the time scale of hours to days.

1.3 Future plans and expected results

For the current experiments, I will further optimize the experimental design, and perform flow-through reactor experiments in which the suspension pH, type of Fe-oxide and the binding form of phosphate (adsorbed versus co-precipitated) will be systematically varied. In a later step, I am planning experiments on the conversion of iron sulphides into iron phosphates and vice versa. During this period, experimental skills will be developed to investigate kinetics and mechanism of P release during sulphidisation of Fe oxides, microscopic and spectroscopic techniques will be trained to characterise iron-containing solids.

1.4 Collaborations (internal / external)

I have a close collaboration with ESR11 (Melanie Münch, Utrecht University) and ESR3 (Victoria Barcala, Deltares), chemical analysis protocols for phosphate, iron and sulfide are modified, unified and shared within these 3 ESRs. Besides, a collaboration between UBT (ESR9, Karel As) and Utrecht is ongoing with shared mineral materials (lepidocrocite) and fitting codes (R script). Eawag (ESR7) and UU (ESR6) currently also submit proposals to various synchrotron facilities to apply for beamtime, in order to ensure continuing access to X-ray absorption spectroscopy (XAS) as a key speciation technique, a shared beamtime at ANKA (Karlsruhe, Germany) is planned on May. In case we would not be allowed to travel to Karlsruhe by that time due to travel restrictions, we will try to send samples to synchrotron facility for analysis if it is feasible.

1.5 Risks and difficulties

Risk is that I might not have enough time to perform experiments and collect data. Time management for my first year should be properly considered with performing experiments, collecting data and teaching assistant. Besides, the situation of coronavirus affects all aspects of our current life. Laboratories are closed, experiments and secondments are postponed. The impacts of this unknown situation still need to be evaluated.

2. Deliverables

Current experiments of ESR6 will contribute to deliverable D1.4. For deliverable D3.1 the ESR plans to learn thermodynamic calculations with modelling program PHREEQC and Stella. Contributions to the deliverables D1.3, D2.1, and D2.2 have not made yet.

3. Training and network activities

3.1 General training events (March 2019 – February 2020)

Event	Date (start – end)	Location (Host)	Objective / expected skills	ECTS points	Contribution	Comments
P-TRAP annual meeting	6/1/2020-10/1/2020	Bayreuth, UBT	Time management, career management, intercultural communication		Poster, Pitch	

3.2 Secondments (March 2019 – February 2020)

Secondment	Date (start – end, planned (when))	Location	Host	Description of work / deviations	Scientific / training (skills) objective	Results and future plans
University of Vienne	Nov. 2020-Dec. 2020 as planned	Vienne, Austria	University of Vienne	Effect organic ligands on Fe mineral transformation	Learn how to design and conduct experiments with taking organic ligand into account	For now I focus on my current experiments, collect samples then I could use Mössbauer spectroscopy for analysis. Since organic ligand part is the next stage of my PhD, I will first finish my current experiments.
University of Bayreuth	Aug. 2021-Sep. 2021 as planned	Bayreuth, Germany	University of Bayreuth	Identification of Fe phases by Mössbauer spectroscopy	Learn how to use Mössbauer spectroscopy for my experiments, and learn how to analyse data	

3.3 Conferences (March 2019 – February 2020)

Conference name	Date (start – end, planned (when))	Location	Presentation (oral / poster)	Title of presentation	Authors (main author + co-authors)	Public available (yes / no) / web link
KNCV meeting	23/01/2020	Utrecht	Participation			

3.4 Data collected, measurement / sampling campaigns (March 2019 – February 2020)

Data	Date (start – end, planned (when))	Location	Description of work	Scientific objective	Samples (nature / number)	Results and future plans
Flow-through reactor	27/01/2020-28/02/2020	Utrecht	Data of flow-through reactor experiments are collected	Observing P release during the reductive transformation of iron minerals in laboratory experiments	Solid samples are collected for future XAS experiments	I will further optimize the experimental design

4. Dissemination activities (March 2017 – February 2019)

4.1 Scientific publications

No scientific publications were done for the period March 2019 – February 2020.

4.1 Project related dissemination activities

No project related publications were done for the period March 2019 – February 2020.

Diffuse phosphorus input to surface waters
- new concepts in removal, recycling and management -

D5.8 P-TRAP – 1st Progress Report

ESR7: Mechanistic studies on the transformation of P-containing Fe(III) oxides

ESR	Ville Nenonen, ville.nenonen@eawag.ch
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Co-supervisor	Erik Smolders (P-TRAP); Lenny Winkel (ETH Zurich)
Non-Academic secondment host	GEOS (Susan Reichel)
Official start – end	01/10/2019 - 30/9/2022

1. Scientific progress

1.1 Project introduction and objectives

Phosphorus (P) is an essential element and often the growth-limiting nutrient in ecosystems. Loading of surface waters with phosphate from agricultural sources is the main cause for the eutrophication of freshwater bodies and associated environmental problems (e.g. Smith et al., 1999). P in soils is present in a variety of refractory (not readily bioavailable) and labile (readily bioavailable) forms. Refractory forms include P in apatite minerals (Ca-phosphate), P co-precipitated with and/or adsorbed onto Fe- and Mn-(oxy)hydroxides, or organic P in particulate organic matter (Filippelli, 2008). Labile P includes phosphate (PO_4^{3-}) dissolved in soil pore water and weakly adsorbed onto soil particle surfaces. In natural waters, P is found in colloidal and dissolved forms. Colloidal P in rivers and lakes is mostly associated with mineral particles and particulate organic matter and is not readily bioavailable, whereas dissolved phosphate is readily bioavailable.

In soils and natural waters, Fe(III)-(oxy)(hydr)oxides (named Fe-oxides in this report) and natural organic matter (NOM) have high densities of binding sites and are therefore prominent sorbent phases (Gerke and Hermann, 1992; Gerke, 1993). The reductive dissolution of Fe-oxides in subsoils and the formation of Fe(III)-precipitates by dissolved Fe(II) oxidation in oxygenated surface waters critically impact on the cycling of P across redox gradients between soils or aquifers and surface waters (Gunnars et al., 2002). Detailed insights into the formation, structure, and chemical reactivity of Fe(III)-precipitates and Fe(III)-NOM-precipitates are essential to understand the speciation of nutrients and contaminants in natural waters and soils. The major cation Ca^{2+} can affect the P-binding by Fe(III)-(NOM-)precipitates (Senn et al., 2015), and also impacts on P cycling via the precipitation of Ca-phosphates or P-containing Ca-carbonates during the oxygenation of anoxic groundwaters, driven by the degassing of CO_2 and the increase in pH when anoxic groundwaters exfiltrate into oxic surface waters (Griffioen, 2006). Ca-minerals are not susceptible to reductive dissolution, and may therefore contribute to longer-term P-binding in less reactive forms.

Within the P-TRAP network, ESR7 will focus on the kinetics and mechanisms of the formation and transformation of P-bearing Fe(III)-precipitates in the presence of interfering inorganic and organic solutes (P, Si, Ca, organic ligands). Specifically, the first focus is to assess how organic compounds in combination with inorganic solutes impact on the composition, structure, phosphate uptake, chemical reactivity and colloidal properties of Fe(III)- and Ca-precipitates formed during Fe(II) oxidation in natural waters. The second focus is to study the structural transformation of fresh Fe(III)- (and Ca-) precipitates over time (precipitate aging) as a function of precipitate type and solution chemistry, with special emphasis on potential P-release and (longer-term) P-trapping in Ca-phases.

Finally, ESR7 also aims at studying the structure and reactivity of P-bearing solids from P-TRAP-field systems to gain complementary mechanistic insights. The findings should provide a basis for a systematic assessment of Fe, phosphate, and OM dynamics in natural water systems.

1.2 Project results

1.2.1 First year

ESR7 started his work in October 2019. A first experiment on the aging of P-containing Fe(III)-precipitates formed in different background electrolytes was performed in October 2019. This experiment was performed in analogy to previous work on the subject (Roberts et al., 2004; Kaegi et al., 2010; Voegelin et al., 2010, 2013; Senn et al., 2015, 2017, 2018), with the aim to gain first experience with experimental and analytical procedures. Fresh Fe(III)-precipitates were synthesized by oxidation of 0.5 mM Fe(II) in bicarbonate-buffered (8 mM HCO_3^-) solutions adjusted to pH 7.0 with CO_2 gas in 200 mL plastic bottles. Experiments were performed at a molar P/Fe ratio of 0.25, in the presence of Na or Ca as background electrolyte cation and without or with Si (molar Si/Fe ratio of 0 or 1.0) (i.e., in four electrolytes referred to as Na, Na + Si, Ca, Ca + Si). Trace amounts of As and Cd were added to the initial solutions to assess their co-transformation during precipitate formation and aging. The oxidation of Fe(II) in the synthetic groundwaters was initiated by spiking Fe(II) into the aerated solutions. For each of the 5 sampling times, 4 h, 1 d, 3 d, 6 d and 10 d, individual reaction bottles were set up. Initial unfiltered and final filtered solutions (0.1 µm; cellulose nitrate membrane) were acidified (1% concentrated HNO_3) and analyzed for element concentrations using inductively coupled plasma - mass spectrometry (ICP-MS). The Fe(III)-precipitates were collected by membrane filtration (0.1 µm; cellulose nitrate) and air-dried for analysis by X-ray absorption spectroscopy (XAS) at the Fe K-edge (synchrotron light source at Karlsruhe Institute of Technology). Light scattering analyses were performed with selected precipitate suspensions using two different methods / instruments to gain experience with analytical protocols.

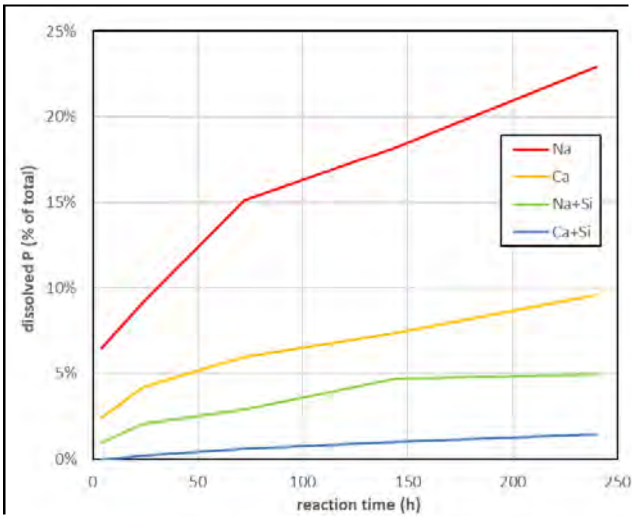

Fig. 1: Fractions of dissolved P as % of total initial P in the precipitate suspensions in Na, Ca, and Na+Si, Ca+Si background electrolytes. The first data after 4 h represent dissolved P concentrations after Fe(III)-precipitate formation, the increase over time is associated with precipitate aging.

Wet chemical analyses (Fig. 1) and synchrotron data show that the composition and structure of the fresh solids collected after 4 h are in line with expectations from earlier work (Senn et al., 2015). On the other hand, phosphate resolubilisation during aging was not as marked as observed in previous work (Senn et al., 2018). Most probably, this difference was due to the fact that the earlier experiments were performed by repeated sampling of the same reaction bottle, allowing for gradual CO_2 outgassing and pH increase. In contrast, the current experiments were performed in gas-tight reaction bottles, which were not opened before sampling, thus minimizing CO_2 release. The outgassing of CO_2 and the associated increase in pH drive the continuing polymerization of Fe(III) as well as the precipitation of Ca-phosphate and Ca-carbonate. The experiment thus highlighted the need to control CO_2 outgassing and pH evolution in future aging experiments.

Although CO_2 outgassing was limited, the solution data (Fig. 1) revealed that aging over 10 days led to the re-solubilisation of precipitated P. In line with our earlier work (Senn et al., 2017, 2018), P re-solubilisation was most pronounced in the Na electrolyte, but decreased in the presence of Si and/or Ca, which enhance both precipitate stability and P retention. For the Na-electrolyte, where initial P removal was lowest and P re-solubilisation highest, XAS showed that the initial precipitate after 4 h reaction time is a mixture of poorly crystalline lepidocrocite and a ferrihydrite-like phase (Fig. 2). The second-shell peak at ~2.7 Å arises from edge-sharing FeO_6-octahedra in lepidocrocite platelets. The slight increase of this peak with time thus points to the ongoing growth of the lepidocrocite crystals with lower P sorption capacity at the expense of ferrihydrite with high P sorption capacity during precipitate aging, explaining the release of P over the aging phase. These analyses help to understand the effects of organic compounds and aging on the structure of Fe(III)-precipitates formed by the oxidation of Fe(II) in natural waters.

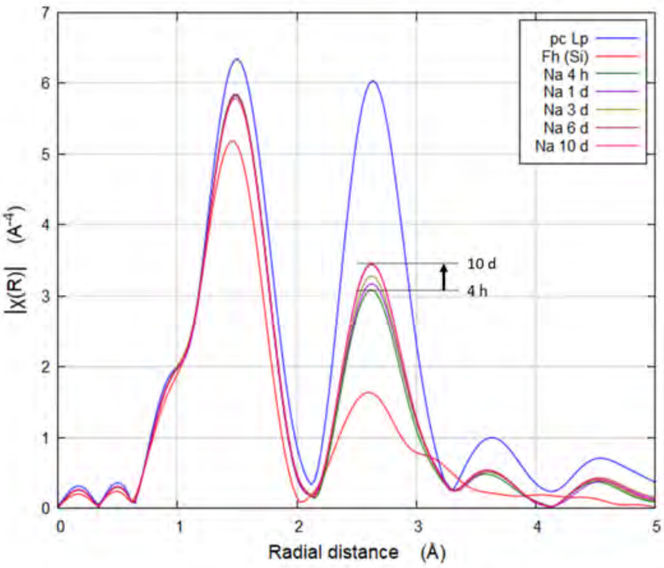

Figure 2. Fourier-transformed Fe K-edge EXAFS-spectra of Fe(III)-precipitates with P/Fe of 0.25 formed and aged in Si-free Na-bicarbonate electrolyte in comparison to reference spectra of poorly crystalline lepidocrocite (pc Lp) and ferrihydrite (Fh (Si)).

The most effective initial P removal and most limited release during aging in the Ca + Si electrolyte can be attributed to Si-induced formation and stabilisation of ferrihydrite with high P sorption capacity and to effective P-binding in amorphous Ca-Fe-phosphate.

The sample solutions were also measured with static light scattering (SLS) and dynamic light scattering (DLS) instruments to determine aggregate sizes in suspension. Aggregate sizes greatly varied with electrolyte cation and Si level, but were in general too high for stable particle suspensions. The use of light scattering measurements thus needs to be further tested, and possibly limited to colloidally stable solids that pass filter membranes.

ESR7 recently started his second experiment on the effect of organic compounds on the formation of Fe oxidation products. Experiments were performed with citric acid, galacturonic acid, polygalacturonic acid (PGA) and leonardite humic acid (LHA) to cover a range in molecular weights, functional groups and structural complexity. Stock solutions of the organic acids were obtained by neutralization with NaOH to pH 7, i.e., with the organic acids in their deprotonated anionic forms. In a first test experiment, the effects of the organic compounds on precipitate formation are tested in Na and Ca electrolytes (in analogy to the aging experiment described above) at a molar P/Fe ratio of 0.25 and with molar C/Fe ratios of 0.6 and 2.4. Initial unfiltered and final unfiltered solutions will be analysed by ICP-MS (Na, Ca, P, As, Cd) as well as by TOC-L-analyser for total organic carbon (TOC). First experience with suspension filtration revealed differences among the different treatments, and showed that solids separation from suspension needs to be further optimized as with some organic ligands the apparent size of the solids was <2µm (colloidally stable) and they thus passed through the membrane (mainly in solutions with citric acid) and no solids were recovered. In the next experiment, ultracentrifuge will be used in solid collection instead. TOC-analyses on the PGA- and LHA-stock solutions confirmed that the macromolecules were fully solubilised at pH 7. Solids will be analysed by Fourier-transform infrared spectroscopy (FTIR) for initial structural characterization.

With respect to planned work on the structure and reactivity of P-containing Fe solids from P-TRAP systems, we received 6 Fe-rich water treatment residues (WTR; fresh and pelletized Fe(III)-sludge and Fe(III)-coated sand) from the P-TRAP project partner AquaMinerals. The samples were air-dried (40°C) and the sands size-fractioned for further analysis. In a first step, a basic characterization for elemental compostion (X-ray fluorescence spectrometry (XRF), digestion), mineral structure (X-ray diffraction, XRD) and specific surface area (SSA, with Brunauer-Emmett-Teller (BET) method) will be performed.

The experiments will yield valuable mechanistic and quantitative information on the solid structures and colloidal properties, which support the development of Fe-based P-trapping and recycling methods within the P-TRAP project. In more general context, the results are expected to advance the understanding of the role of Fe(III)-precipitates in environmental nutrient and trace element cycling.

1.3 Future plans and expected results

In continuation of the experiments performed thus far, the next steps are:

- Consolidation of experimental setup and analytical procedures to assess effects of organic compounds on Fe(III)-precipitates formation and performing a set of experiments.
- Consolidation of experimental setup and analytical procedures to assess effects of aging on Fe(III)-precipitates structure and P retention and performing of a set of experiments.
- Characterization of Fe(III)-solids from P-TRAP systems (Fe(III)-solids from waterworks used in P-TRAP systems, Fe(III)-solids from soils treated with water treatment residues).

In the second half of 2020, synchrotron analyses at Angströmquelle (ANKA; Karlsruhe Institute of Technology, Germany), SOLEIL (University of Paris-Saclay, France), and/or at Swiss Light Source (SLS; Paul Scherrer Institute, Switzerland) are foreseen on samples from laboratory experiments and field systems.

In terms of the development of academic and transferable skills, plans for the next reporting period include training of scientific writing and presentation skills and attendance of the TSTC 2 in Utrecht (July 2020), participation in teaching activities at Eawag/ETHZ, and attendance of courses in the doctoral programme of ETHZ. Scientific presentations are planned at the PhD student congress of the Institute of Biogeochemistry and Pollutant dynamics (IBP, ETHZ, April 2020), in the Eawag department seminar, at the Swiss Geoscience Meeting (SGM, November 2020) and at P-TRAP meetings.

1.4 Collaborations (internal / external)

Collaboration with Aquaminerals (P-TRAP NAPO) was initiated by receiving different water treatment residues (WTR) for structural characterization and experiments on reactivity. Fe-sludges and Fe-coated sands were dried and the plan is to prepare subsamples from larger batches for X-ray diffraction (XRD) and X-ray fluorescence (XRF) measurements to compare the mineralogy and elemental composition of the samples. Collaboration with the secondment partners (Erik Smolders in KUL and Leonard Osté in Deltares) will take place during the next reporting period. A collaboration is also planned with Gerwin Koopmans from the University of Wageningen (Netherlands). In continuation of a field study on the use of Fe(III)-sludge for P immobilization in soils performed in Wageningen (Koopmans et al., 2020), the same soils should be resampled to assess the longer-term (6-7 years) structural transformation of the applied Fe(III)-sludge and lasting impacts on P availability.

1.5 Risks and difficulties

The structural characterization of Fe(III)-solids from laboratory and field systems also involves the use of synchrotron-based spectroscopies. Access to the respective infrastructure is bases on competitive beam-time proposals, and the rejection of proposals or loss of beam-time due to technical problems at the synchrotron during the beam-time could result in delays.

2. Deliverables

Deliverables associated with the project of ESR7 are (with due date in project months in parentheses):

D1.1: Novel granular materials and characterization of their properties (30).
D1.3: Guidelines and recommendations for retaining and recovering Fe-bound P in drainage system (40)
D1.5: Guidelines and instructions for the application of Fe & P containing solids for soil amelioration (42).
D3.1: Kinetic models for the transformation of P containing Fe phases (36).
D3.2: Report on the fate of P during Fe phase transformations (40).

The started characterization of WTRs from AquaMinerals and the initiated work on the effect of organic compounds on fresh Fe(III)-precipitates will contribute to deliverable D1.1 in the future, to a certain extent also deliverables D1.3 and D1.5. The initiated experiments on precipitate aging and P retention will provide experimental results relevant for completing deliverables D3.1 and D3.2.

3. Training and network activities

3.1 General training events (March 2019 – February 2020)

Event	Date (start – end)	Location (Host)	Objective / expected skills	ECTS points	Contribution	Comments
P-TRAP TSTC1 and meeting	6.-10.1.2020	Bayreuth	Meeting other participants of the P-TRAP. Getting training in scientific writing, intercultural communication etc.	-	Poster about my project	
Chemistry Grundpraktikum	13.-20.1.2020	ETH Zurich	Gain teaching experience, meet PhD students from same institute and familiarize with lab protocols relevant to own work.		Teaching BSc students in environ. sciences in a laboratory practical;	
German A1 course	1.10.-15.12.2019	Eawag	Learn basics in German			

3.2 Secondments (March 2019 – February 2020)

No secondments have been conducted during the first year of the project. The secondments listed below are currently planned for the second project year, but timing also depends on the progress with own laboratory experiments.

Secondment	Date (start – end, planned (when))	Location	Host	Description of work / deviations	Scientific / training (skills) objective	Results and future plans
Deltares	June-July 2020	Deltares, Utrecht	Leonard Oste	Collection of particulate / colloidal Fe(III) solids from drainage ditches (waters, sediments). Sampling of soils treated with Fe-rich WTR (collaboration	Collect Fe(III)-solids from P-TRAP field sites, for structural / compositional characterization to complement laboratory experiments (Fe(III)-solids from ditches as "fresh" solids,	

				with Gerwin Koopmans, WUR).	soils with aged WTR as "aged" solids).	
KULeuven	June 2020	KUL, Leuven	Erik Smolders	Run AF4-ICP-MS analyses on colloidal Fe(III) suspensions from laboratory experiments on role of organic compounds.	Training in AF4-ICP-MS method for Fe-colloid characterization; gain results relevant to experiments on Fe(III)-NOM-precipitates.	

3.3 Conferences (March 2019 – February 2020)

Conference name	Date (start – end, planned (when))	Location	Presentation (oral / poster)	Title of presentation	Authors (main author + co-authors)	Public available (yes / no) / web link
Swiss Geoscience Meeting	November 2019	Fribourg, Switzerland	No own contributions			
1st P-TRAP meeting	January 2020	Bayreuth, Germany	Poster	Formation and transformation of iron(III) and calcium precipitates: Consequences for phosphate trapping	Ville Nenonen, Ralf Kaegi, Stephan Hug, Lenny Winkel, Andreas Voegelin	no

3.4 Data collected, measurement / sampling campaigns (March 2019 – February 2020)

Data	Date (start – end, planned (when))	Location	Description of work	Scientific objective	Samples (nature / number)	Results and future plans
ICP-MS	Oct 2019 Feb 2020	Eawag	ICP-MS analyses on solutions from laboratory experiments	Gain information on concentrations of dissolved solutes	aqueous solutions from laboratory experiments.	
XAS	Oct. 2019	ANKA, Karlsruhe	Synchrotron XAS analyses on solids from laboratory experiment on precipitate aging.	Gain information on structure of Fe solids.	Fe(III)-precipitates from laboratory aging experiments.	

4. Dissemination activities (March 2019 – February 2020)

4.1 Scientific publications

No scientific publications were done for the period March 2019 – February 2020.

4.1 Project related dissemination activities

No project related publications were done for the period March 2019 – February 2020.

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ESR8: The effectiveness of vivianite as a sustainable Fe and P fertilizer for agricultural crops

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Non-Academic secondment host	Dr. Christoph Hartmann; GEOTEAM; christoph.hartmann@geoteam-umwelt.de
Official start – end	12.02.2020 – 11.02.2023

1. Scientific progress

1.1 Project introduction and objectives

The project is dedicated to the study of the effectiveness of vivianite as a source of P and Fe fertilizer for agricultural crops. Vivianite which is obtained from the precipitation of P from waste waters is a poorly soluble compound and may be a potentially useful and sustainable source of P and Fe for crop growth and production. The research of ESR 8 will quantify the effect of the application of vivianite to soils in comparison to conventional fertilizers with respect to yield, bioavailability and crop quality. This will be carried out in collaboration with ESR 2 and 10. The project will also establish the dosage of vivianite and other Fe-P minerals required for obtaining similar bioavailability and plant nutritional status as with conventional fertilizers. The project is a significant part of the work package 1 which is specifically looking into closing the cycle of phosphorus application in agriculture.

1.2 Project results

1.2.1 First year

Due to majorly administrative and immigration challenges, I am able to start at the University of Seville just this month (February, 2020) and just commencing my first experiment while undergoing laboratory training at the University. I have also commenced preliminary literature review on the topic of my research. The details of my first experiment are summarized below:

The objective of the experiment is to test different synthetic vivianite product as a source of P in an artificial growing media (a mixture of calcareous sand and sea sand). Cucumber seeds were raised in a nursery on 28th January 2020 and transplanted on 18th February 2020. I do not have data or any result about this experiment yet as it has just started.

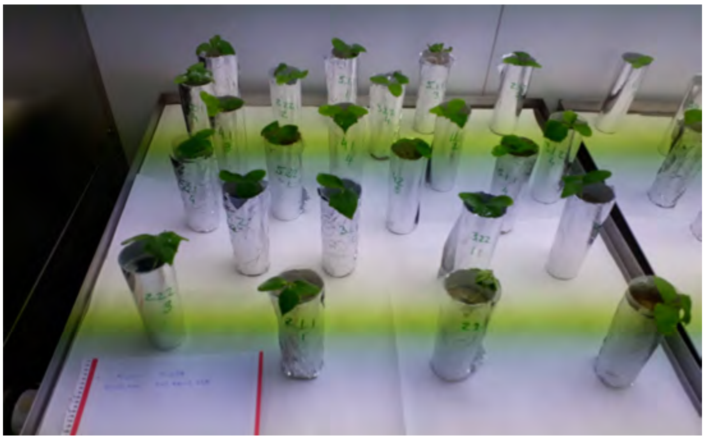

Fig. 1: Growth experiment using cucumber seeds on different vivianite products

1.3 Future plans and expected results

The plans both scientific and training for the next reporting period are centred on developing basic skills in research management, looking into new expertise in areas related to my field of research from soil fertility to agronomy, and improve on my scientific communication skills.

Scientific plans include:

1. Testing vivianite from different sources (synthetic, Fertiberia, Aquaminerals) as a P and Fe source for plants in pot experiments involving different kind of soils. At different stages, this will include:
   a) First approach to the potential P fertilizer of vivianite by estimating P supply to plants in pot experiments in different growing media: calcareous sand, and two different soils. This study will be performed by using synthetic vivianites.
   b) Comparing the P and Fe fertilizer effect of different products (vivianite and P rich Fe (III) compounds) from different origin (synthetic, from water purification) in soils by means of pot experiments.
2. Study of the effect of different application methods on the efficiency of vivianite applied as fertilizer: powder, suspension in water, and granules.

In all the cases, we will compare the efficiency and apparent recoveries of applied P as vivianite and P rich Fe particles with soluble mineral fertilizers, and in the case of Fe with Fe chelate (EDDHA-Fe). Bioavailability of applied P and Fe will be assessed in the soil after application by means of availability indices (e.g. Olsen P and hydroxylamine extractable Fe) and chemical fractionation. Residual effect of applied products will be assessed by consecutive bioassay in the same pots.

Training plans include:

1. Science school (Coupling of Fe and P dynamics on global and microscopic scale) - Utrecht University (July 2020).
2. Transferable skills Training course 2 (E-learning modules as dissemination channels) at Utrecht University (July 2020).

1.4 Collaborations (internal / external)

No collaboration has been performed during this reporting period within the P-TRAP consortium.

- For the next one, within the consortium it is planned with Fertiberia and Aquaminerals for testing its vivianite as fertilizer products.
- If products from microbial transformations obtained in the University of Manchester are available, they will be included in different experiments.

1.5 Risks and difficulties

The implementation of my work plan has been delayed due to visa challenges and hence I started about five months later than other ESRs.

2. Deliverables

ESR8 is involved in deliverable D1.4, D1.5, D3.1, D3.2. First test for deliverable D1.5, the selection of relevant soil types for which the effect of adding P containing Fe phases, have been started. No contribution for the other deliverables yet.

3. Training and network activities

3.1 General training events (March 2019 – February 2020)

Event	Date (start – end)	Location (Host)	Objective / expected skills	ECTS points	Contribution	Comments
TSTC 1 - Being a scientist in the 21st century (D4.1) and 1st P-TRAP annual meeting	6th -10th Jan, 2020	University of Bayreuth, Germany	To learn basic requirements for carrying out a successful doctorate degree.	-	Presenting a pitch and poster about my project.	It was a well-planned out event and, in the future, the ESRs could be involved in the planning of similar trainings.

3.2 Secondments (March 2019 – February 2020)

Secondment	Date (start – end, planned (when))	Location	Host	Description of work / deviations	Scientific / training (skills) objective	Results and future plans
Investigating effect plant exudates on mobilization of Fe in soils.	July 2020	Vienna, Austria	Prof. Dr. Stefan Kraemer (University of Vienna)	Study of organic ligands effects on P and Fe release from vivianite.	Acquisition of experience on the effect of plant mobilizing mechanisms on P and Fe uptake	Organic ligands will increase P and Fe release from studied fertilizers; potential effects on bioavailability of this nutrients assessed

3.3 Conferences (March 2019 – February 2020)

ESR8 has not participated in any conferences.

3.4 Data collected, measurement / sampling campaigns (March 2019 – February 2020)

ESR8 has no data collected so far due to the late start of experimental work.

4. Dissemination activities (March 2017 – February 2019)

4.1 Scientific publications

No scientific publications were done for the period March 2019 – February 2020.

4.1 Project related dissemination activities

No project related publications were done for the period March 2019 – February 2020.

ESR9: Studying the effect of Fe addition to sediments on the sedimentary biogeochemical processes

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Non-Academic secondment host	Gerard ter Heerdt + (Gerard.ter.Heerdt@waternet.nl)
Official start – end	01-09-2019 till 01-09-2022

1. Scientific progress

1.1 Project introduction and objectives

Lakes are an important fresh water source in times of water scarcity and often have a dual function as important recreational areas during summer. Unfortunately, the (over)use and discharge of fertilizers has resulted in a build-up of phosphate rich lake sediments which, when released, are able to cause large algae blooms in spring and summer. Algae blooms can interfere with the mentioned uses as toxins produced by these organisms make drinking this water and swimming in it harmful for the health.

Regulations have been put into place that attempt to moderate the fertilizer application in the field and therewith reduce release of phosphate unto surface waters. Although this is certainly helpful, a problem remains with legacy P or phosphorus present in the sediment. Legacy P is phosphorus that has built up in the lake sediments and becomes accessible due to seasonal fluctuations in dissolved oxygen levels. At high oxygen concentrations iron oxides will allow to bind the phosphorus coming from the sediment. In contrast, at low oxygen concentrations iron will become reduced and this diminishes its capacity for phosphorus binding. Phosphorus is thus released from the sediment and this will stimulate the growth of algae. Therefore, algae blooms can even be observed in lakes where nowadays hardly any phosphorus discharge happens. The lake sediment is said to be stuck in a cycle of release and fixation. Application of more iron could be a key way to fix phosphorus in the sediment and break this cycle.

In this project we will investigate 1) which phosphorus species or associations are associated with low P-release during anoxic conditions in a field site, 2) the phosphate adsorption capacity of iron oxide coated sand, 3) the fate of the added iron in the sediment, 4) which conversion rates determine the longevity of the iron oxide coated sand barrier and 5) effects of iron addition on the biogeochemistry in the sediment. In the end we would like to understand how the different elemental cycles (S, P, Fe and organic molecules) are correlated and determine effectiveness of iron application in the capture of phosphorus in the sediment. P-TRAP is focused on these same research themes.

In the other projects these same themes come forward but are more oriented towards engineering, chemical mechanisms or plant growth. In this project, together with ESR 11 we focus on a specific fresh water system that is very important for life quality. Lakes will become more important as a water source as summers will become drier and more unpredictable in the future. In times of need it will be essential to be able to use water from lakes to irrigate agriculture land on which we depend. Mitigating harmful algae blooms will play a key role in keeping this source available.

1.2 Project results

1.2.1 First year

A large part of the initial period has been spent on getting acquainted with the methods we would like to use in the analysis of sediment biogeochemistry. These, for now, being: 1) sediment core taking and slicing, 2) photospectrometry to determine iron, phosphorus, ammonium and sulfate in porewater of the sediment, 3) micro-sensor profiling to determine pore concentrations of oxygen, pH and sulfide, 4) sequential extraction to analyse the solid-phase of the sediment (in cooperation with ESR 11), 5) mineral characterisation by x-ray diffraction analysis (XRD), Fourier-transformed infrared spectroscopy (FTIR) and surface area measurement and 6) creating a sediment-incubation set-up in which anoxic conditions can be applied and efficacy of iron application monitored.

Field Work

So far, we have contacted the local water authority Wasserwirtschaft Ansberg. Permission was asked and received to use the partially eutrophic Brombachsee reservoir as our field site and for sediment extractions. This artificial reservoir contains a highly eutrophic small settling lake (Kleiner Brombachsee, area of 2 km^2, Fig.1) which is separated by a dam from a deeper main lake (Grosser Brombachsee, area of 12 km^2). This lake suffers less from harmful algae blooms.

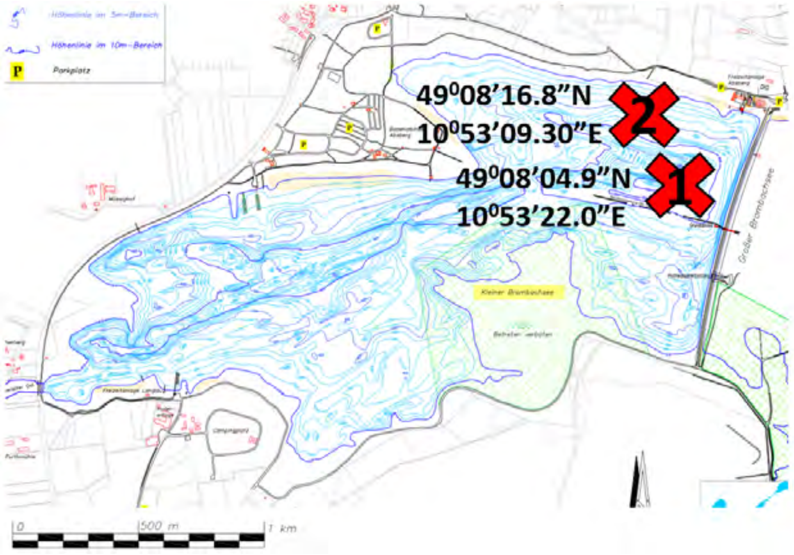

Fig. 1: Bathymetric map of Kleiner Brombachsee and locations with GPS data of exploratory cores taken. Location 1 was at latitude 49^{0}08’04.9” and longitude 10^{0}53’22.0” and location 2 at latitude 49^{0}08’16.8” and longitude 10^{0}53’09.30”

In this lake we have taken out 2 exploratory cores. The cores were sliced and pore water concentrations of sulfur, iron and phosphate were investigated (Fig. 2). The cores were both considerably reduced with oxygen penetration depths of just 7 mm. As SO_4 reduction rates and oxygen penetration depth are negatively correlated it is no surprise that sulfide concentrations were high in both locations. Peaks of sulfide up to 150 µM were observed. In location 1 sulfide levels were lower than for location 2. As iron and sulfide precipitate as metastable FeS we found that iron concentrations are consequentially higher in location 1. The precipitation of FeS can also be observed in the porewater profiles of the sulfide and iron. Free phosphate concentrations are considerable

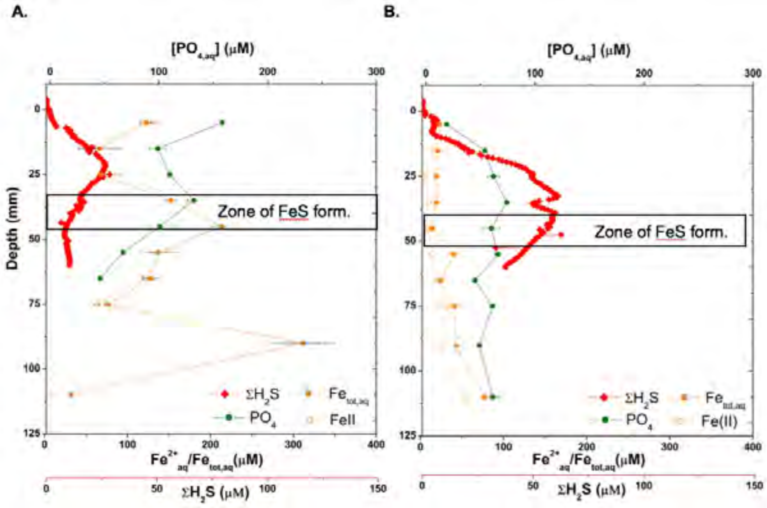

Figure 2: Pore water concentrations in sediment cores from Kleiner Brombachsee. Determined species were: ortho-phosphate PO_4 (●), total iron Fe_{tot} (■), Ferrous iron Fe^{2+} (□) and total sulfide $\sum H_2S$ (◊) for A) location 1 and B) location 2.

in the pore waters of both cores. Ranging from 50-150 µM in location 1 and up to 100 µM in location 2. Clearly there is a phosphate efflux from the sediments into the overlying water. Solid-phase samples were stored in oxygen-free atmosphere and will be analysed for different phosphate species by a sequential extraction method. This will be performed in collaboration with ESR 11 in Utrecht. In this way we ensure that our methods of solid-phase characterization will be similar and the results comparable. The sediment-incubation experiments and fieldwork will be greatly expanded once these techniques have come to full fruition. In this way we will better understand which solid-phase phosphorus is primarily released in the lake water and which are responsible for sediment p-retention.

Furthermore, we will be able to determine efficacy of iron addition for sediment from multiple locations retrieved in different seasons. In this way we will find which phosphorus phases are most responsible for release and retention. Hence, we can develop iron-based addition strategies to increase sediment P-retention.

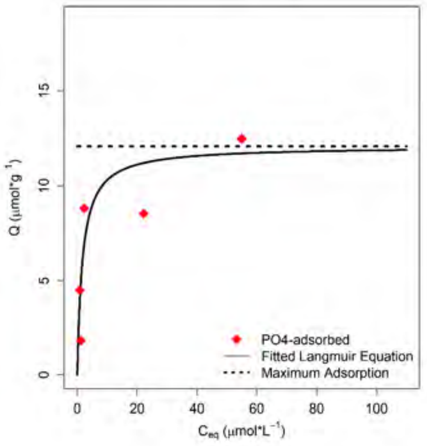

Fig. 3: Adsorption isotherm of iron-coated sand from a water purification sand filter. The isotherm was fitted using the Langmuir equation.

Adsorption isotherm of Iron Coated Sand

From Aquaminerals (non-academic partner organisation) we received iron coated sand. We dried the sand and made an initial characterisation of its adsorption capacity. This was performed by batch adsorption experiments with differing initial concentrations of phosphate. Data was subsequently fitted using the Langmuir model (Fig. 3).

Based on the Langmuir model of adsorption the maximum adsorption of the iron coated sand was determined to be 12 µmol*g^{-1}. These iron coated sands will later be used in the sediment incubation experiments to observe effects on P-release from the sediment. The sand still has to be investigated for elemental composition, organic matter content, surface area and mineral character.

Lab experiments to get acquainted with techniques: schwertmannite adsorption kinetic analysis

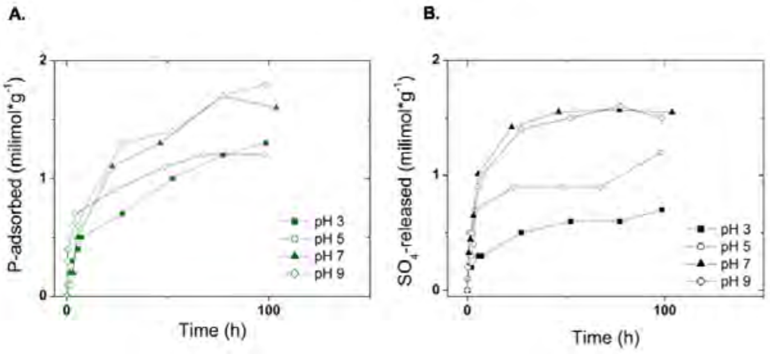

Fig.4: a) PO_4-adsorption unto Schwertmannite under differing pH conditions b) The associated SO_4-release.

To get acquainted with photospectrometric techniques as well as FTIR we performed experiments to characterize phosphate adsorption onto Schwertmannite under different pH. Schwertmannite is a mineral formed under acidic sulfate-rich conditions, mainly acidic mine drainage sediment. The iron-sulfate hydroxide is metastable and releases more sulfate as pH is increased. This results in behaviour counter-intuitive to that of stable iron oxides containing no sulfate. Namely that anion-adsorption is greatest at low pH. A kinetic experiment was performed to observe this effect (Fig. 4).

As can be observed, higher pH has more favourable phosphate adsorption kinetics. Interestingly, the same pattern is observed for sulfate release (Wang et al. 2015). It has been observed that pH causes a difference in complexation of the sulfate in schwertmannite. At high pH sulfate is more weakly bound

as an outer-sphere molecule whereas at lower pH it is more strongly bound in the structure as an inner-sphere molecule. This means that ligand exchange will be easier at higher pH as is clearly observable in our data. This leads us to propose the following adsorption and ligand exchange reactions as relevant:

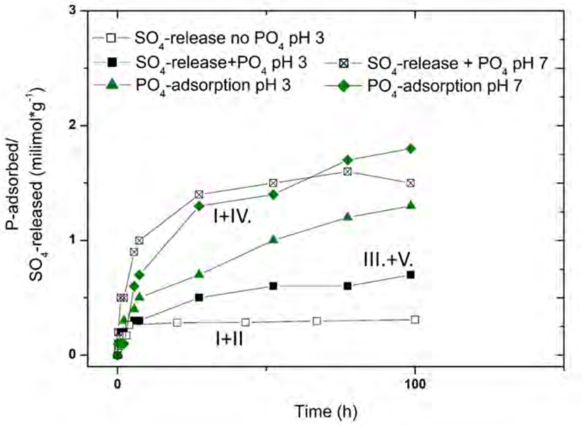

Fig. 5: Graph combining phosphate adsorption and sulfate release for pH 3 and 7. The roman numerals indicate which reactions would primarily take place at the given pH conditions.

Sulfate complexation changes

I. $[\mathrm{SHM{=}SO_4}]_{\mathrm{inner}} \rightarrow [\mathrm{SHM{=}SO_4}]_{\mathrm{outer}}$ ●*equil. moves to right at high pH*

II. $[\mathrm{SHM{=}SO_4}]_{\mathrm{outer}} \rightarrow [\mathrm{SHM{=}X}]_{\mathrm{outer}} + [\mathrm{SO_4}]_{\mathrm{aq}}$ ● *equil. moves right at high pH*

Ligand exchange reactions

III. $[\mathrm{SHM{=}SO_4}]_{\mathrm{inner}} + \mathrm{H_xPO_4}^{3-x} \rightarrow [\mathrm{SHM{=}PO_4}]_{\mathrm{inner}} + [\mathrm{SO_4}]_{\mathrm{aq}}$ ●*slow rate*

IV. $[\mathrm{SHM{=}SO_4}]_{\mathrm{outer}} + \mathrm{H_xPO_4}^{3-x} \rightarrow [\mathrm{SHM{=}PO_4}]_{\mathrm{outer}} + [\mathrm{SO_4}]_{\mathrm{aq}}$ ●*fast rate*

Hydroxyl adsorption

V. $[\mathrm{SHM{=}OH}] + \mathrm{H_xPO_4}^{3-x} \rightarrow [\mathrm{SHM{-}OH{=}H_xPO_4}^{3-x}$ ●*equil. moves to left at high pH*

So, during our kinetic experiment we arrive at different kinetic areas depending on which pH we have (Fig. 5).

1.3 Future plans and expected results

Monitoring Lake Brombachsee

Every two to three months we will return to Lake Brombachsee to monitor the release and fixation of phosphorus within the sediment. This will allow us to gain a better understanding of seasonal fluctuations. Furthermore, we would like to do statistical analysis to see which phosphate species, as determined by sequential extraction, correlate with reduced $\mathrm{PO_4}$-release from the sediment.

We expect that his will help to us to give new ideas to more efficiently bury phosphorus in the sediment.

Sediment incubation experiments

We will incubate sediment in the lab at controlled temperature and will add iron coated sand to the cores. Subsequently overlying water will be bubbled with nitrogen to mimic anoxic bottom waters in lakes. After a certain period of anoxia, we will slice the core and analyse pore water profiles of $\mathrm{PO_4}$, $\mathrm{H_2S}$, Fe, $\mathrm{NH_4}$, $\mathrm{SO_4}$ as well as perform sequential extraction. Interesting will also be to reapply oxygen to observe possible hysteresis effects. We expect that the Iron-coated sand will prevent $\mathrm{PO_4}$ to reach the overlying water but we do not expect an alteration in the sediment biogeochemistry. Furthermore, we hypothesise that longevity of the iron-oxide barrier will depend on organic carbon quality and content as well as sulfate reduction rates.

Investigation of organic-iron-phosphorus complex

A highly under-investigated natural ternary complex is formed by humic acids, iron-ions and phosphate. In certain situations, these complexes can be a significant sink for phosphate and one that might be rather resilient to oxidation processes. It would be interesting to attempt to design synthesis experiments of these complexes. This will teach us about the conditions required to form these types of complexes and will allow to perform stability experiments.

1.4 Collaborations (internal / external)

Collaboration microbiology department Bayreuth University

Name: Corinna Sachs (corinna.sachs@uni-bayreuth.de)

Corinna Sachs is a PhD student who works on Cable Bacteria which grow in seasonally anoxic basins containing high sulfide concentrations. Cable bacteria oxidize sulfide and reduce oxygen. Quickly they deplete available sulfide and subsequently they form long filaments that conduct electrons from the deeper sulfidic layers toward the oxic zone. As the Kleiner Brombachsee is a seasonally anoxic basin containing sulfide the right environment for growing these bacteria are present. During a preliminary sediment incubation, the characteristic geochemical profile induced by these bacteria was already observed. In the future we will go out again together to take sediment samples.

Objectives: The microbiology department has granted us access to use the micro-sensors for sulfide, pH and O_2 measurement. Furthermore, we could greatly enhance each other`s research as our department can characterize the geochemistry of the sediment that is being incubated. On the other hand, the microbiology department could greatly contribute in characterizing the microbial community present in the Brombachsee sediment as well as incubation experiments.

Expected Results: We expect to find enrichment of iron and sulfate reducing bacteria and sulfide oxidizing bacteria in the sediment under anoxic conditions. Furthermore, we will gain an understanding of the dynamics.

Planned: In May we will go to the Brombachsee to take cores together.

Collaboration Utrecht University with ESR 11

Name: Melanie Münch (m.a.munch@uu.nl)

Melanie and me work both on lakes albeit in different countries with both lakes having their own characteristics (shallow vs. deep, ground-water influx and efflux). Our general research themes greatly overlap, however accents might greatly differ depending on the situation we find in our lake characteristics.

Objectives: Initially, to benefit from the expertise of our faculties. Utrecht has a long and rich experience in sequential extraction techniques. Bayreuth University has its expertise in sulfur speciation as well as Mossbauer Spectroscopy. Exchange of these techniques will be the first thing to do. Later on, we can greatly learn from each other`s experience in the field and design the sediment-incubation set-ups as well as future mesocosm experiments together. Exchanging the results and comparison will be a large part of the collaboration. Also we will start to develop a model together for the intertwined elemental cycles observed in sediments.

Expected Results: We expect to develop a working mathematical model for the lake sediment and to gain a better understanding of Fe-P burial in sediments.

Planned: From 09-03-2020 till 20-03-2020, I ,ESR 9, will come to Utrecht University to be introduced into sequential extraction techniques.

1.5 Risks and difficulties

As all of Europe suffers under the corona virus so did the research of the last few weeks. A field work trip we had planned in Utrecht, namely from 16/03/2020 till 20/03/2020 has been cancelled. Also, a field work trip to the Kleiner Brombachsee in the week of 23/03/2020 till 27/03/2020 has been cancelled as the Wasserwirtschaftsamt Ansberg has cancelled all its collaborations with third parties for the time being. For this time, we will focus on further enhancing the kinetic model for phosphate adsorption unto schwertmannite, completing the sediment-incubation set up and writing a literature review on phosphate dynamics in lake sediments. The duration of the corona virus regulations still remains to be seen.

Other more general risks and difficulties are that as I`m lacking a driver`s license I will require people to go along with me on sampling trips. This requires careful planning and good will of my colleagues.

2. Deliverables (full text)

D2.2 Strategy for achieving long-term P burial in lake sediments by Fe addition: The main focus of the P-TRAP project is to use iron containing by-products to stably bind phosphates in the sediment. Our first focus will therefore be in the application of spent iron-coated sands from water purification plants (supplied by AquaMinerals). Of these coated sands we determined the phosphate adsorption isotherm. In the near future we will apply these iron-coated sands to the sediment-incubation cores to investigate efficacy in P-binding and stability of these sands in the sediment. Next to this we also have practiced the production of iron-oxide minerals in the lab. In a later stage we might try to apply these as well. Another important research angle in the strategy will also consist of identifying P-phases that are at present strongly associated with P-burial. If one could induce more phosphate to be bound to these phases stable burial might also be achieved.

D2.4 Report on long-term effects of Fe addition to lakes: Literature has been read on previous Fe-additions in order to restore lakes. Some of which were successful and others who were unsuccessful. Identifying the differences in manner of application and lake characteristics will allow for assessment of long-term effects of Fe addition. In addition, we will cooperate with ESR 11 who will do field work on lakes that have been previously treated with iron salts.

D 3.2 Report on the fate of P during Fe phase transformations: So far, the sediment-incubation set-up is not quite ready. However, we have been designing the sediment-incubation set-up. Including: the way redox cycles will be applied and how the phase transformations will be assessed. We expect to make big progress in this deliverable after returning with the knowledge on sequential extraction from Utrecht. Furthermore, we will also rely on the knowledge gained in the more chemistry-oriented projects to cooperate in this deliverable, being ESR 6, 7 and 10.

3. Training and network activities

3.1 General training events (March 2019 – February 2020)

Event	Date (start – end)	Location (Host)	Objective / expected skills	ECTS points	Contribution	Comments
Spectroscopic Methods **Lectures and practicals**	01/10/19 - 01-02-2020	University of Bayreuth	1) Being able to interpret spectra from a variety of spectroscopic techniques. 2) Getting acquainted with the quantum mechanical background of spectroscopy.	6	Participant, joined in practica	This course has helped me to be able to interpret FTIR spectra in the lab. Furthermore, it has exposed me to a variety of methods that could be used.
Guiding Master Student for a 3 week research module	20-02-2020	University of Bayreuth	Learn how to give guidance and motivation to a student.	-	Daily guidance	Especially communication is something that is greatly practiced in this way.
P-TRAP training	06/01/2020	University of Bayreuth	Get to know fellow P-TRAP members and acquire new ideas and insights for future research.	-	Participant	A good first meeting to meet all supervisors and exchange views and ideas.

3.2 Secondments (March 2019 – February 2020)

Secondment	Date (start – end, planned (when))	Location	Host	Description of work / deviations	Scientific / training (skills) objective	Results and future plans
University Utrecht	09/03/2020 – 20/03/2020	Utrecht	ESR 11	Exchange of technique on sequential extraction for solid-phase P analysis	Learning a new method and standardize the method to reach comparable results	Learned a new method.
University of Manchester	October 2020	Manchester	ESR 5	Introduction into microbial community analysis. Sample preparation, preservation and analysis.	Learning a new method to analyse microbial community composition.	Ability to apply microbial methods in my own research project.

3.3 Conferences (March 2019 – February 2020)

Conference name	Date (start – end, planned (when))	Location	Presentation (oral / poster)	Title of presentation	Authors (main author + co-authors)	Public available (yes / no) / web link
BayCEER conference	16/10/2019	Bayreuth	No	None	None	none

3.4 Data collected, measurement / sampling campaigns (March 2019 – February 2020)

Data	Date (start – end, planned (when))	Location	Description of work	Scientific objective	Samples (nature / number)	Results and future plans
	24-01-2020	Kleiner Brombachsee	Taking cores to analyse solid phase and pore water.	Make a first exploration of the sediment biogeochemistry of an eutrophied lake.	4 cores sliced into 10 slices each.	The lake contained a large concentration of sulfide. And showed clear characteristics of a highly reduced sediment
	05/03/2020	Biopolymer institute Bayreuth	Taking scanning electron microscopy (SEM) images of the iron coated sands	Investigating shape and structure of the sand and gaining a first impression of the elemental composition of the lake.	Photo`s and count% of elemental composition.	

4. Dissemination activities (March 2017 – February 2019)

4.1 Scientific publications

No scientific publications were done for the period March 2019 – February 2020.

4.1 Project related dissemination activities

No project related publications were done for the period March 2019 – February 2020.

References

Wang, X., Gu, C., Feng, X., Zhu, M.: Sulfate local coordination environment in Schwertmannite, Environ. Sci. Technol. 2015, 49, 10440−10448, 2015, https://doi.org/10.1021/acs.est.5b02660

P-TRAP

Diffuse phosphorus input to surface waters
- new concepts in removal, recycling and management -

D5.8 P-TRAP – 1st Progress Report

ESR 10: Biogeochemical mechanisms influencing the bioavailability of P and Fe from vivianite

ESR	Rouven Metz, Rouven.metz@univie.ac.at
Supervisor	Stephan Krämer, Stephan.kraemer@univie.ac.at
Co-supervisor	Walter Schenkeveld, w.d.c.schenkeveld@uu.nl
Non-Academic secondment host	Javier Branas, jbl@fertiberia.es
Official start – end	01.09.2019 – 31.8.2022

1. Scientific progress

1.1 Project introduction and objectives

The research at the University of Vienna (ESR10) is primarily focused on determining the rates and mechanisms of Fe and P mobilization from vivianite, a promising natural fertilizer, and the role of the geochemical environment on this process. In addition, the effect of secondary mineral precipitation and naturally occurring Fe binding ligands (including low molecular weight organic acids, siderophores and humic substances) on the rates of vivianite dissolution will also be mechanistically and quantitatively determined. State of the art analytical tools combined with geochemical modeling will be used to unravel the mechanisms involved. The project will be accomplished in close collaboration with international partners including secondments (for ESR) at academic (Eawag, Switzerland and Utrecht University, Netherlands) and industrial host (Fertiberia, Spain) with in the P-TRAP project partners.

1.2 Project results

1.2.1 First year

1.2.1.1 Vivianite alteration

Vivianite, a hydrous ferrous iron phosphate ($Fe_3(PO_4)_2 \cdot 8H_2O$), occurs worldwide in many reducing environments *e.g.* lakes, rivers, swamps, waterlogged soil, and sewage sludge, as well as in marine systems (Rothe et al., 2016). Despite its widespread occurrence, the importance of vivianite for the burial of P and its role in the global P cycle might have been underestimated so far (Egger *et al.*, 2015). In recent years, vivianite received more and more attention both as a sink to lower P loads of water bodies and also, as a valuable resource itself (Rothe et al., 2016; Wilfert et al., 2016; Wu et al., 2019).

Vivianite is the Fe-rich end-member of the vivianite mineral group with the general formula $Me_3(XO_4)_2 \cdot 8H_2O$, where Me is divalent Mg, Mn, Fe, Co, Ni, Cu, Zn, and X can be P or As (Capitelli et al., 2012). Isomorphous substitution in this group occurs readily, and intermediate compositions are often observed (Frost et al., 2004). Vivianite is composed of single (Fe_I) $FeO_2(H_2O)_4$ and double (Fe_{II}) $Fe_2O_4(H_2O)_4$ octahedral sites which are linked by PO_4 tetrahedra, thus building sheets. These sheets are weakly held together by hydrogen bonds between the H_2O ligands, explaining the perfect cleavage (010) of vivianite (McCammon and Burns, 1980; Rouzies and Millet, 1993).

Vivianite can oxidize rapidly due to self-catalytic oxidation, air oxidation, and possibly also by photocatalytically induced oxidation (Frost et al., 2004). The appearance turns from colourless to light-blue, and further blue to deep-purple with increasing degree of oxidation. The short distance between the Fe atoms in site II enables the charge transfer from $Fe^{2+} \rightarrow Fe^{3+}$ between these edge-shared Fe octahedra as a homonuclear intervalence transition, which explains the origin of the colour (McCammon and Burns, 1980). The oxidation of Fe^{2+} to Fe^{3+} ions is balanced in the crystal by a simultaneous conversion of H_2O ligands to OH^- ions (McCammon and Burns, 1980). This leads to the destruction of the hydrogen bonds and a subsequent collapse of the vivianite structure. The oxidized vivianites thus, show a flaky habit parallel to (010) (Moore, 1971). The dehydration and oxidation processes take place preferentially at the surface of cleaved vivianite sheets, and are supported by the layered structure of vivianite, due to easy diffusion (Hanzel et al., 1990). However, the oxidation process showed a non-Arrhenius behaviour, thus there is not just a single activation barrier and the process is not only diffusion controlled. Hanzel et al. (1990) suggested, that the oxidation is progressively hindered by its product, since Fe^{3+} disturbs the layered structure and thus the oxygen diffusion into the vivianite lattice. McCammon and Burns (1980) observed in their study an incongruent site-specific oxidation with a dependence on the actual degree of oxidation. They argued, that the intervalence transition stabilizes the $Fe^{2+}-Fe^{3+}$ pair of site II against further oxidation. While at the beginning of the oxidation Fe_{II}^{2+}/Fe_{I}^{2+} concentration ratio equals 2:1, the concentration of stabilized Fe_{II}^{2+} increases with the degree of oxidation and thus the Fe_{II}^{2+}/Fe_{I}^{2+} ratio increases rapidly due to a preferential oxidation of the Fe_{I} site (McCammon and Burns, 1980).

While the initial oxidation of vivianite proceeds fast, and it is not sure if pure Fe^{2+}- vivianite could exist in natural environments, the oxidation slows down and tends to stabilize at ca. 50%, which corresponds to the limit of stability of the monoclinic vivianite structure (Rouzies and Millet, 1993). If oxidation exceeds 50%, the triclinic Fe^{2+}/Fe^{3+} phosphate hydrate metavivianite is formed, which was first described by Ritz et al. (1974). Finally, when all Fe is oxidized, the amorphous phase santabarbaraite is formed (Pratesi et al., 2003). Thus, the full sequence can be shown as: monoclinic vivianite → triclinic metavivianite → amorphous santabarbaraite.

However, while the proposed oxidation sequence is based on laboratory condition, the application of vivianite as fertilizer requires knowledge of the mechanisms and rates which are environmentally relevant. Therefore, the geochemical factors: pH, redox potential and soil solution composition are of high relevance. Voegelin et al. (2010) showed in their study about the aeration of Fe(II)-containing waters, how Ca^{2+} and Si influenced the precipitation of Fe(III)-phosphates and thus the formation of minerals. Moreover, soils are complex systems, thus, not only the solution composition influences the dissolution and alteration of vivianite, but also the gas and the solid phase. Roldán et al. (2002) mimicked the sequestration of P during the oxidation of vivianite, and the resulting mineral was not amorphous santabarbaraite, but crystalline lepidocrocite. Also, vivianite itself might not be present in its pristine state, but with isomorphous substitutions, what effects the crystal lattice.

Additionally, (micro)organisms impact the alteration of vivianite. In general, the bioavailability of P and Fe in soils is low. P is taken up by plants and microorganisms from soil solution in the inorganic form of $H_2PO_4^-$ and HPO_4^{2-}. Field crops generally require > 0.2 mg P/L for optimal growth (Borch and Fendorf, 2007). Natural sources are P containing minerals and the mineralization of organic matter. The availability of P is strongly reduced by the formation of Ca-phosphate if pH > 6.5, by the sorption to Fe-/ Al-oxides/hydroxides if pH < 5.5, and by the formation of Al- and Fe-phosphates if pH < 4.5. Furthermore, Fe(III) (hydr)oxide minerals, the most abundant P sorbents, have a poor solubility and slow dissolution kinetics at circum-neutral pH (Kraemer et al., 2006). Thus, (micro)organisms evolve several mechanisms to increase the bioavailability of Fe and therefore also the bioavailability of adsorbed P. The secretion of protons for proton-promoted dissolution, of reductants for reductive dissolution and the secretion of ligands for ligand-controlled dissolution, are such mechanisms (Kraemer, 2004). Also, synergistic effects between reductants and ligands have been shown (Schenkeveld et al., 2016). However, the effect on the oxidation of Fe(II)-phosphate vivianite has not been examined so far.

ESR 10's work in P-trap is aimed at a mechanistic and quantitative understanding of the main processes regarding the oxidative dissolution of vivianite in soils. The determination of dissolution rates and secondary minerals under environmental relevant conditions will provide the fundamental knowledge for the applicability of vivianite as Fe and P fertilizer. Which will follow the idea of a circular economy: starting with the reduction of P loads of waters and using the byproduct vivianite as P source for fertilization.

Research questions

- What are the rates and mechanisms involved in Fe and P mobilization during oxidation of vivianite?
- What is the effect of the geochemical environment on the oxidative dissolution of vivianite?
- Which secondary minerals form and what are their effects on the oxidative dissolution of vivianite?
- What is the quantitative effect of naturally occurring Fe-binding ligands on the oxidative dissolution of vivianite?

Hypotheses

It is hypothesized that vivianite is a good Fe and P fertilizer, since the oxidation of vivianite leads to destabilization of the mineral structure, enabling plants to acquire P and consequently, poorly crystalline secondary Fe(III) mineral phases can also serve as Fe source. The composition of the soil solution specially the ratio of Fe to Ca^{2+} and Si influences the resulting secondary mineral phase by interfering the crystallization (Voegelin et al., 2010). Additionally, natural organic ligands, exuded by plants and microorganisms enhance this process, by further destabilizing the mineral, sequestering Fe and releasing PO_4^{2-} in soil solution. The overall process however, is slow enough to maintain a single application of fertilizer over several years and prevents P wash out.

1.2.1.2 Experimental

I) Synthesis of Vivianite

Several different batches of vivianite were synthesized. Attempts were made to produce minimally oxidized vivianite by modifying standard protocols and also to obtain different particle size and hence, surface area to compare the reactivity.

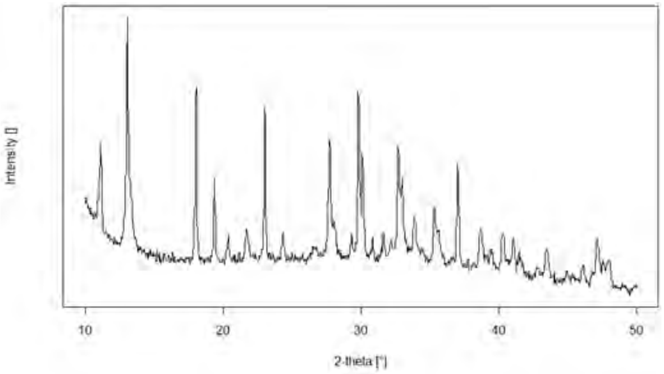

Fig. 1: X-ray powder diffraction (XRD) of synthesized vivianite

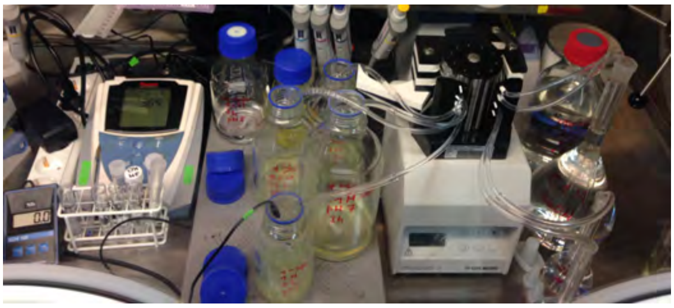

Fig. 2: Effect of the synthesis parameters on the properties of vivianite. Four factors: titration speed, molarity of NaOH, reaction time and pH, were tested for the influence on the crystallinity of vivianite.

Vivianite was synthesized according to the protocol of Al-Borno and Tomson (1994) under N_2 environment (O_2 0.0%) using an anoxic chamber (mBRAUN, unilab 7185). All solutions were prepared using anoxic water obtained by bringing ultrapure milli-Q water (18.2 MΩ·cm, TOC < 2 ppb) to boil and purging with pure N_2 while cooling down (~ 2hrs). Two solution were prepared, $NaH_2PO_4 \cdot H_2O$ (0.36 M) with KH_2PO_4 (0.04 M) as P-source and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (0.6 M) as Fe^{2+} source. The solutions were slowly mixed under constant stirring. With the addition of 0.5 M NaOH, a whitish/ bluish precipitate formed readily. The pH was consistently measured throughout the synthesis (Orion 3 star, Thermo) and remained around 3.5. The suspension was stirred for ~5 hrs, vacuum filtered (filter paper, 5-8 µm Whatmann), washed and dried inside the glovebox. Mineral purity was determined by X-ray powder diffraction analysis (PANalytical X'pert Pro), confirming vivianite as the only crystalline phase (Fig. 1).

Table 1: Experimental design of vivianite synthesis

#	speed mL/min	NaOH [M]	time [h]	pH
1	30	0.1	3	5
2	1	1	3	5
3	1	0.1	72	5
4	1	0.1	9	7
5	1	0.5	24	7

In the first experiment, the effect of the synthesis parameters (titration speed, molarity of NaOH, reaction time, and pH) on the properties/crystallinity of vivianite was determined. (Fig). Therefore, 0.1, 0.5, or 1 M NaOH were pumped using a peristaltic pump with rates of 1 mL/min or 30 mL/min in the previously mixed P-Fe-solution until the desired pH, 5, 6 or 7 was reached. The total reaction time was 3, 24 or 72 h. Afterwards the precipitates were vacuum filtered, washed and dried inside the glovebox. The experimental design can be seen in Table 1.

II) Vivianite oxidation

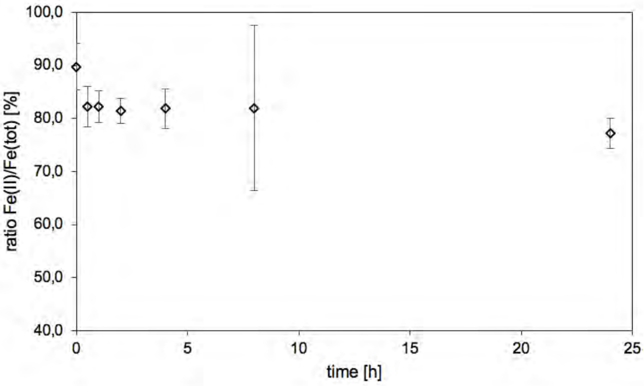

Fig. 3: Dry vivianite oxidation over time measured by Fe(II)/Fe(total) ratio

As soon as the synthesized vivianite came in contact with oxygen, an immediate colour change from light blue to dark blue/ purple was evident. The extent of oxidation was measured by the Fe(II)/Fe(tot) ratio with the ferrozine-assay (Stookey, 1970),using UV−vis spectrophotometer (Varian Cary 50) at a wavelength of 562 nm. As indicated by the colour change, a rapid oxidation of ~ 10% occurred within the first 30 min, while the process slowed down over time and after 24 h the total oxidation of the initial value was 13% (Fig. 3). These findings are consistent with Hanzel et al. (1990), who suggested, that the oxidation is progressively hindered by its product, since Fe^{3+} disturbs the layered structure and thus, the oxygen diffusion into the vivianite lattice.

III) Raman characterization of Vivianite

Dried synthetic vivianite powder in its pristine and oxidized form was analyzed with Raman spectrometer (Horiba Jobin Yvon LabRAM-HR Evolution spectrometer) using 473/532/633 nm laser. Due to the very high sensitivity of vivianite against the laser beam extreme care had to be taken. The blue laser line was chosen with low intensities, resulting in longer runs. After each run, the sample was checked for reddish radiation damage. Nevertheless, with the normal-oxic setup only broadened peaks with a slight shift to higher wavenumbers could be obtained, indicating a disturbed or amorphous structure (Fig. 4, “oxidized vivianite”).

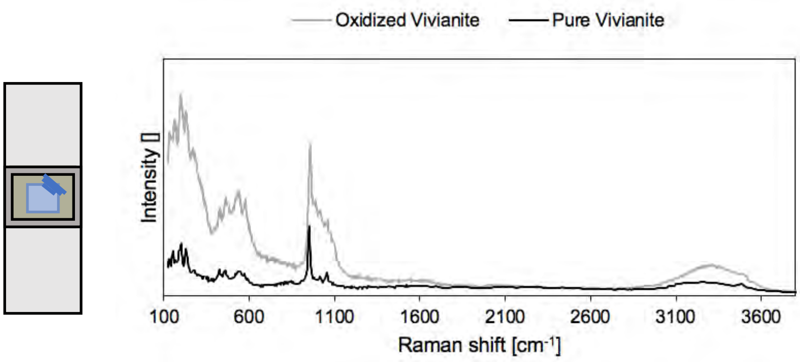

Fig. 4: Right: Raman spectra of oxidized and pure vivianite. Left: sketch of the setup for the measurement of pure vivianite, consisting of: Object slide, tape, cover slip, Kapton tape - building a small anoxic chamber

Thus, a small anoxic chamber was designed and fabricated in house that allowed raman measure-ments under inert (N_2) environment without the interference of O_2. Also, higher laser power could be used with this setup, and no radiation damage was observed thereafter.

The characteristic sharp peak at 950 cm^{-1} at the PO stretching region, the pattern between 100 to 600 cm^{-1} of the OPO bending as well as the broad peak of the OH streching region between 2700 to 3700 cm^{-1} was obtained.

IV) Preliminary Oxidative Dissolution Experiments of Vivianite at natural relevant pH

Lab synthesized vivianite was incubated under oxic and anoxic conditions at environmentally relevant pH (4 - 8) for 41 days. Briefly, 1.99 mM vivianite suspension with 0.01 M NaCl background electrolyte was adjusted with 0.5 M HCl or NaOH to the desired pH. The pH was buffered with 0.005 M of either PIPPS (pH 4 and pH 8), NaOAc (pH 5), MES (pH 6), or MOPS (pH 7). All batches were prepared anoxically and one set was brought to oxic conditions immediately to compare oxic and anoxic dissolution. The experimental vials were light protected with aluminium foil while suspensions were agitated constantly with stirring bars.

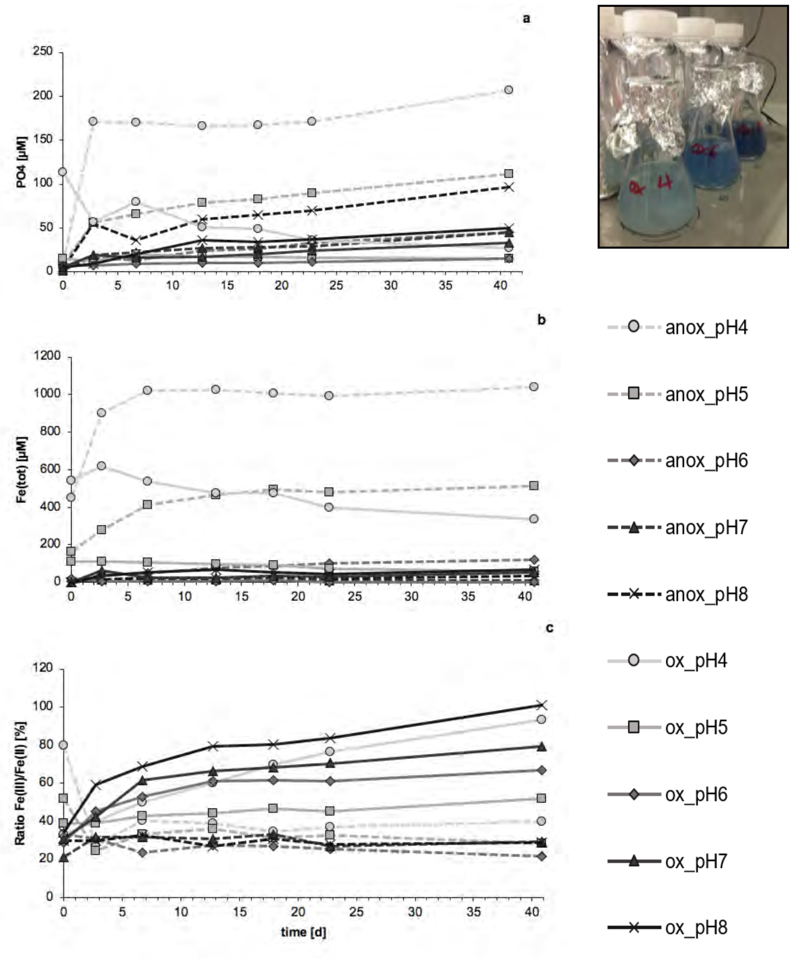

Fig. 5: a) PO_4 concentration in solution over time b) Fe(tot) concentration in solution over time c) "Oxidation of vivianite", ratio of Fe(III)/Fe(II) of solids.

At each sampling point, pH was measured, suspension as well as filtered (CA, 0.45 µm) samples were retrieved, stabilized in 6 M or 1 M HCl respectively and stored in the fridge (4 ºC) until analysed. Samples were analysed for Fe(II), Fe(tot) and PO_4 in the filtrate and the suspension. Additionally, a suspension sample was taken, centrifuged, decanted, and dried in the glovebox for solid phase analysis. For Fe speciation, stabilized, and dissolved samples were measured by ferrozine-assay (Stookey, 1970), according to Porsch and Kappler (2011) with UV−vis spectrophotometer (Varian Cary 50) at 562 nm. Phosphate concentrations were determined by molybdenum-blue method (Murphy and Riley, 1962) with FIA-070, version 2.1 (FIAlyzer-1000, FIAlab). In addition, Fe(tot) and P were also measured by ICP-OES for additional check.

The dissolution and oxidation of vivianite was highly pH dependent (Fig. 5). While the dissolution increased with decreasing pH, the oxidation showed contrasting behaviour. Thus, the highest concentration of PO_4 (207 µM) and Fe(tot) (1000 µM) in solution was measured in samples with pH 4. The

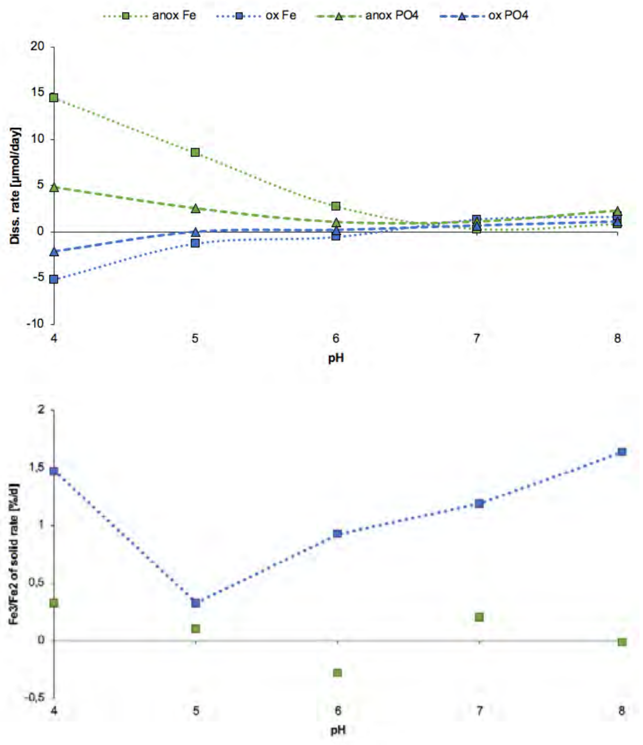

Fig. 6: Top: Dissolution Rate (0-41 days) over pH. Calculated from Fe(tot) and PO_4 in solution. Bottom: “oxidation rate”, ratio of Fe(III)/Fe(II) of solids per time.

samples with the highest Fe(III) concentration of solid particles, was incubated at pH 8 (100%). The oxidation remained constant at the initial level of ca. 30% for the anoxic samples, and increased constantly with time for the oxic samples. In contrast, a high initial dissolution was observed, which levelled off with time or even decreased for oxic samples at lower pH, resulting in a negative dissolution rate (Fig. 6).

The overall mobilization of PO_4 and Fe was much higher in anoxic samples than in oxic setups, except for pH 4. Thus, it is assumed that in the oxic batches, oxidation occurred and new amorphous Fe(III)-phases have been formed, which do not stay in solution and probably sorb the previously released PO_4. This would also explain why XRD did not detect any other crystalline phases than vivianite, even after 42 days of incubation. Moreover, the adsorbed PO_4 might interfere and hinder the formation of new crystalline Fe(III)-phases, similar to the findings of Roldán et al. (2002). Microscopic observations are expected to provide further understanding of these processes.

Summary

We were able to synthesize pure vivianite without the surface oxidation (No Fe(III) was measure (detection limit <5 µM). We confirmed the mineral purity by XRD, and in house developed a sampling stage to measure vivianite powder non-destructively and anoxically with Raman spectroscopy.

Within first experiment, we tried to vary the crystallinity of vivianite to investigate the effect on the mobilization of Fe and PO_4, in order to be able to provide base for the most suitable way of vivianite conversion and fertilizer production. The oxidation of dried vivianite was followed over time and the oxidation and dissolution rate of vivianite at environmentally relevant pH was investigated.

We could observe a strong pH dependence due to protonation of PO_4 at low pH, and a deprotonation of PO_4 at the surface with a structural Fe-oxidation at higher pH values. Also, we assume that the released PO_4 hinders the formation of crystalline secondary Fe(III) phases, which explains the missing signal in XRD.

1.3 Future plans and expected results

Vivianite, with various variation (particle size, Fe(II) ratio, crystallinity) will be synthesized and thoroughly characterized in our lab. The effect of geochemical environment (pH, redox potential, soil solution composition, O2 partial pressure, naturally occurring Fe-binding ligands, humic substances and sequestration of P) on the oxidative dissolution of the vivianite, release of P and Fe and secondary mineral formed will be tested in batch as well as flow through column experiments. Experimental data will be complimented by geochemical modelling tools to achieve a molecular scale mechanistic and quantitative understanding of these processes.

Experimental samples will be analysed for their chemical properties as the P:Fe(II) ratio, using ferrozine and molybdenum blue method as well as ICP-OES/MS analysis. The surface area will be measured *via* BET measurements. Particle size and crystal morphology will be determined with electron microscopy combined with chemical mapping with EDX-detector. Mineral phases and crystallinity will be determined by XRD and RAMAN spectroscopy. The latter will also be applied to measure gradual oxidative alterations of vivianite in a non-destructive manner using in house developed sample stage. Synchrotron-based analytical techniques might be used to study local coordination and structure of Fe(II)/(III)-PO_4-phases.

1.4 Collaborations (internal / external)

No internal or external collaborations started yet.

1.5 Risks and difficulties

No risks or difficulties were faced.

2. Deliverables

ESR 10 is involved in the deliverables D1.4, D1.5, D3.1, D3.2.

WP1: Several different batches of vivianite were synthesized. Attempts were made to obtain vivianite with minimum oxidation during synthesis, and also to obtain different particle size and hence, surface area to compare the reactivity. We have provided this synthetic vivianite to our partners at KUL to further test it’s applicability in soil systems.

WP3: Oxidative dissolution experiments of vivianite at natural relevant pH (4 – 8) have been conducted. Solid phase was characterized with XRD, Raman and for Fe2/Fe3 ratio by ferrozine method.

3. Training and network activities

3.1 General training events (March 2019 – February 2020)

Event	Date (start – end)	Location (Host)	Objective / expected skills	ECTS points	Contribution	Comments
TSTC1	06.01.2020 – 10.01.2020	University of Bayreuth	Being a scientist in the 21st century, 1st Annual Meeting	-	Participation, poster	
Mineralogical phase analysis	17.10.2019 – 27.1.2020	University of Vienna	Hands-on experience XRD, RAMAN Spectrometry	5	Participation, exam	
Topics in Environmental Geosciences and Geoecology	13.10.2019 - 27.1.2020	University of Vienna	Actual topics in env. geosciences	-	Participation	
Environmental Interface Geochemistry	3.3. – 30.6.2020	University of Vienna	In-depth understanding of interface geochemistry	3	Participation, exam	
HTML course	6.3.2020	University of Vienna	create a website	-	Participation	
Introduction to R	9.3. – 10.3.2020	University of Vienna	Statistical program R	-	Participation	
R advanced	6.5. – 7.5.2020	University of Vienna	Statistical program R	-	Participation	

Chemical accidents/ first aid	11.5.2020	University of Vienna	Laboratory safety	-	Participation	
Introduction to Python	8.6.2020	University of Vienna	Programming language	-	Participation	
Remediation of contaminated sites	3.3. – 30.6.2020	University of Vienna	Remediation techniques	10	Participation, exam	

3.2 Secondments (March 2019 – February 2020)

Secondment	Date (start – end, planned (when))	Location	Host	Description of work / deviations	Scientific / training (skills) objective	Results and future plans
EAWAG	1.8.2020, 2021, 2022	Zürich, Switzerland	EAWAG	Characterise products of vivianite transformation by X-ray absorption spectroscopy	Advanced spectrometry	
Fertiberia	1.4. 2021 – 31.6.2021	Madrid, Spain	Fertiberia	Studies of Fe and P mobilization from commercial vivianite (as produced by FERTIBERIA) fertilizers in comparison to model vivianite phases.		
UU	1.10.2021 – 31.12.2021	Utrecht, Netherlands	UU	Numerical geochemical modelling involving kinetics of P and Fe release from vivianite.		

3.3 Conferences (March 2019 – February 2020)

Conference name	Date (start – end, planned (when))	Location	Presentation (oral / poster)	Title of presentation	Authors (main author + co-authors)	Public available (yes / no) / web link
EGU	2021	Vienna, Austria	poster			
Goldschmidt	2021	Lyon, France	poster			
EGU	2022	Vienna, Austria	Oral			
Goldschmidt	2022	Chicago, USA	Oral			

3.4 Data collected, measurement / sampling campaigns (March 2019 – February 2020)

Data	Date (start – end, planned (when))	Location	Description of work	Scientific objective	Samples (nature / number)	Results and future plans
Ox-VivDis-spH4_8	05.11.2019 – 15.01.2020	University of Vienna	Oxic dissolution of vivianite at natural relevant pH	Dissolution rates of vivianite at different pH	Liquid, solid	Strong pH dependence
DryVivOx	28.1.2020 – 30.1.2020	University of Vienna	Oxidation of vivianite in dry state	Dry oxidation of vivianite	solid	Fast initial oxidation
XRD	-	University of Vienna	Characterization of vivianite		solid	Confirmation of crystalline solid phases
Raman	-	University of Vienna	Development of measurement method and characterization of vivianite	Following the oxidation degree of vivianite	solid	Confirmation and oxidation of crystalline and amorphous phases
VivSynth	05.02.2020 – 08.02.2020	University of Vienna	Vivianite was synthesized with varying titration	Influence of synthesis on resulting material	Liquid, solid	

			speed, base conc., stirring time, pH			
AccVivOx	24.02.2020 – 04.03.2020	University of Vienna	Vivianite was incubated in solution and oxidation was accelerated by H2O2, heat, air purging, anoxic control	End product of oxidation	Liquid, solid	Completely oxidized vivianite, Amorphous P-Fe(III)-phases
StdViv	12.03.2020 -	University of Vienna	Synthesis and characterization of vivianite standard stock material	Standard material	Liquid, solid	

4. Dissemination activities (March 2017 – February 2019)

4.1 Scientific publications

No scientific publications were done for the period March 2019 – February 2020.

4.1 Project related dissemination activities

No project related publications were done for the period March 2019 – February 2020.

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P-TRAP

Diffuse phosphorus input to surface waters
- new concepts in removal, recycling and management -

D5.8 P-TRAP – 1st Progress Report

ESR11: Effects of Fe supplementation on the ecology and P dynamics in eutrophic lakes

ESR	Melanie Münch, m.a.munch@uu.nl
Supervisor	Dr. Thilo Behrends / t.behrends@uu.nl
Co-supervisor	Prof. Dr. Stefan Pfeiffer / s.pfeiffer@uni-bayreuth.de
Non-Academic secondment host	Waternet, Gerard ter Heerdt / gerard.ter.heerdt@waternet.nl
Official start – end	01/01/2020 – 31/12/2023

1. Scientific progress

1.1 Project introduction and objectives

Nutrient overload and especially overload with phosphorous (P) is a major problem for the ecological status of many lakes worldwide leading to algal blooms, loss of biodiversity and poor water quality. The addition of iron (Fe) to these lakes as a measure to bind and bury P in the sediment has already been used as a restoration technique in the past. However, the processes triggered by this Fe-addition in the sediments along with the long-term effects is yet poorly understood. ESR 11 thus aims for an in depth understanding of the biogeochemical processes taking place in the sediment upon Fe-addition to be able to evaluate Fe-addition to lakes as a restoration strategy and to come up with a reliable recipe to be used by the water authorities.

Further, Fe-containing by-products of drinking water production out of ground water are investigated for their suitability for Fe-addition. The use of these by-products would contribute to a circular economy and the recycling of resources.

1.2 Project results

1.2.1 First year

My contract started January 1st 2020, thus by end of February 2020 I was at the first P-Trap meeting, read literature and installed myself at Utrecht University. My project is aimed at finding a technique for the restoration of lakes that are eutrophic due to P overload by addition of Fe-sludge from drinking water treatment. To achieve this, it is crucial to understand the Fe and P dynamics in the lake sediments and to assess, whether the application of Fe-oxides (Fe sludge) can effectively stop the reflux of P form the sediment to the water column. There are some lakes in the Netherlands, which have been treated with Fe before that will serve us as case studies for the long-term effect of Fe addition. In collaboration with WaterNet, a Dutch water authority, we additionally aim to do field experiments to assess the effects of Fe addition on the trophic status of eutrophic lakes.

To be able to investigate the Fe and P dynamics in the sediment, knowledge has to be gained about the present P and Fe pools and their diagenesis. Sequential extractions are well tested methods in soil and marine sciences for this purpose. SEDEX is the method of sequential extraction of P developed by Ruttenberg (1992) and further adjusted by Slomp et al. (1996). SEDEX distinguishes 5 pools of P, loosely adsorbed or exchangeable P, Fe-bound P, authigenic and Ca-bound P, detrital P and organic P. I was trained on SEDEX beginning of February by a fellow PhD student at UU and will pass on that training to ESR9 and ESR3 in March. Further I was trained on core slicing and pore water analysis by my supervisor. Further training on sequential extraction of Fe and S are planned.

For end of February I planned the first field campaign to the lake complex Reeuwijkse Plassen in the Netherlands, to collect cores and surface water samples and measure primary productivity. The Reeuwijkse plassen are a lake complex of shallow, well mixed peat lakes, that have received Fe-treatment in the past. Investigations on these lakes have already been started at UU in the course of a master thesis. Unfortunately, due to the actual situation (Corona) this field campaign has been postponed.

1.3 Future plans and expected results

In 2020 we are planning to start seasonal sampling at Reeuwijkse Plassen which have been selected because they were treated with Fe in the past to remediate for elevated P concentrations in the water column. The aim is to gain insight into the Fe / P coupling in the sediment and the benthic P fluxes in order to determine the crucial parameters for Fe treatment of lakes and to long term effects of Fe treatment. Ideally, after one year we will have a manuscript on that work ready.

To determine crucial parameters for Fe and P coupling in sediments and the influence on bioavailable P in the water column, a diagenetic model will be developed. Ideally, this will be done in collaboration with a Master student, starting in 2020. The data collected for Reeuwijkse Plassen as well as the data collected by ESR 9 will be used to validate the model.

1.4 Collaborations (internal / external)

ESR 9 (Karel As, UBT): Since or projects are closely related, Karel and me collaborate on a regular basis on lab and fieldwork methods, interpretation of results, interesting literature etc. Karel will come to Utrecht to learn the SEDEX method for sequential P extraction out of sediments in March and to support me during the field work.

I am also closely collaboration with ESR 3 and Deltares in general on fieldwork techniques, lab techniques, collaboration with Dutch water authorities and the use of Dutch monitoring platforms.

Long-term collaboration with Waternet and Rijnland, two water authorities of the Netherlands which monitor and manage Dutch lakes have been initiated on March 26th with a Kickoff meeting at the UU. During that meeting further collaboration and secondments have been discussed.

1.5 Risks and difficulties

No difficulties so far.

2. Deliverables (full text)

ESR 11 is involved in the deliverables D1.3, D2.4, and D3.1.

D1.3 – guidelines and recommendations for retaining and recovering Fe-bound P in drainage systems

From my side, so far no guidelines or recommendations could have been developed. However, tools to assess the role of Fe and P in the geochemical processes taking place have been learned and field activities targeted at creating knowledge about the prevailing mechanisms have been designed and planned.

D2.4 – report on long term effects of Fe addition to lakes

The necessary tools to assess the effects of Fe addition on lakes have been agreed on, including sequential extraction of sediment cores to assess Fe and P interaction, diagenesis and burial and core incubation experiments to assess the P flux from the sediments as well as the development and use of a diagenetic model to identify the key factors of Fe – P interaction.

Training in sequential extraction techniques was successfully completed. Fieldwork to retrieve sediment cores for the further investigation of lakes that have been treated with Fe in the past as well as core incubation experiments have been planned and will be executed in the next reporting period.

An already existing diagenetic model will be examined for suitability and further developed together with ESR 9 in the next reporting period.

D3.1 – kinetic models for the transformation of P containing Fe phases

No contribution so far.

3. Training and network activities

3.1 General training events (March 2019 – February 2020)

Event	Date (start – end)	Location (Host)	Objective / expected skills	ECTS points	Contribution	Comments
PTrap TSTC 1	6.-10.1.20	UBT	Time management, intercultural collaboration, outreach, team building among ESRs	-	Poster, Presentation, planning of outreach	
MCT	23.1.20	UU	meeting the Dutch env. chem. community, networking	-	participant	Symposium on environmental chemistry
Geochemistry seminar	6.2.20	UU	Introduction of ESR 11 to the UU earth sciences community	-	presentation	
SEDEX training	3.-7.2.20	UU	Training on sequential extraction of P in sediments	-	participant	
SEDEX training	9.-13.3.20	UU	Training on sequential extraction of P in sediments	-	Teaching ESR 9 and ESR 3	

3.2 Secondments (March 2019 – February 2020)

Secondment	Date (start – end, planned (when))	Location	Host	Description of work / deviations	Scientific / training (skills) objective	Results and future plans
Assesing microbial communities in sediment	October 2020	Manchester	UNIMAN	Lecture and lab training on molecular microbiological techniques to characterise microbial communities	Molecular microbiological techniques. theory, microbial communities and their function Lab methods Data interpretation	
S speciation, diagenetic and reactive transport modelling	September 2021	Bayreuth	UBT	Not yet defined.		
Remediation of lakes by Fe addition / consultancy /	To be determined in March 2020	The Netherlands	Water-Net	Development of a strategy of Fe addition for lake remediation, possibly including consultancy on lake remediation, reviewing of monitoring data	Application of scientific results for water management purposes	

3.3 Conferences (March 2019 – February 2020)

Conference name	Date (start – end, planned (when))	Location	Presentation (oral / poster)	Title of presentation	Authors (main author + co-authors)	Public available (yes / no) / web link
MCT	23.1.20	Utrecht	-	-	-	-

3.4 Data collected, measurement / sampling campaigns (March 2019 – February 2020)

No data have been collected so far.

4. Dissemination activities (March 2017 – February 2019)

4.1 Scientific publications

No scientific publications were done for the period March 2019 – February 2020.

4.1 Project related dissemination activities

No project related publications were done for the period March 2019 – February 2020.

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