CL:AIRE's INSPIRATION bulletins describe practical aspects of research which have direct application to the management of contaminated soil or groundwater in an agricultural context. This bulletin describes the demonstration and evaluation of iFLUX technology to monitor contaminant spreading on a site in The Netherlands.

Use of a novel integrated passive flux sampler to monitor the spreading of solutes in groundwater

1. Introduction

The increasing interest in the spreading of solutes in a groundwater system shows the need for *in situ* flux determination techniques (ITRC, 2010; Newell *et al*., 2011; Triplett Kingston *et al*., 2012; Brooks *et al*., 2018). Especially in the frame of contaminated site management and agricultural land management, contaminant mass fluxes (mass of contaminants passing per unit time per unit area) and contaminant mass discharges (sum of all mass fluxes across an entire plume control plane) are being considered.

Current methods for the determination of spreading or flux of solutes in groundwater use no direct measurements but only simulations based on concentration measurements and Darcy velocity estimations (OVAM, 2004). This entails large uncertainties which cause remediation failures and higher costs for contaminated site owners. On top of that, the lack of useful data makes it difficult to get approval for a risk-based management approach (McKnight *et al*., 2010; Verreydt *et al*., 2012).

Unlike traditional concentration measurements, passive mass flux measurements allow simultaneous exploration of speed and direction of subsoil contaminant spreading. Furthermore, the measurement takes place over a certain period. This guarantees more certainty about the dispersion risks of soil and groundwater contamination, and can help to lower remediation costs. Passive flux measurements are currently seen as the way to go for future spreading risk assessment and remediation optimisation.

2. Study Site

The iFLUX technology was demonstrated and evaluated in 2019 at an urban study site in The Netherlands. The site is contaminated with petroleum hydrocarbons and chlorinated solvents. The iFLUX field campaign focused on the primary pollutants perchloroethylene (PCE), trichloroethylene (TCE) and the degradation products cis+trans-1,2-dichloroethylene (DCE) and vinyl chloride (VC). Multiple source zones resulted in a large plume (> 400 m) under a city centre. Previous source zone remediation action took place in 2018. Current actions include the monitoring of the plume until a stable end situation is reached.
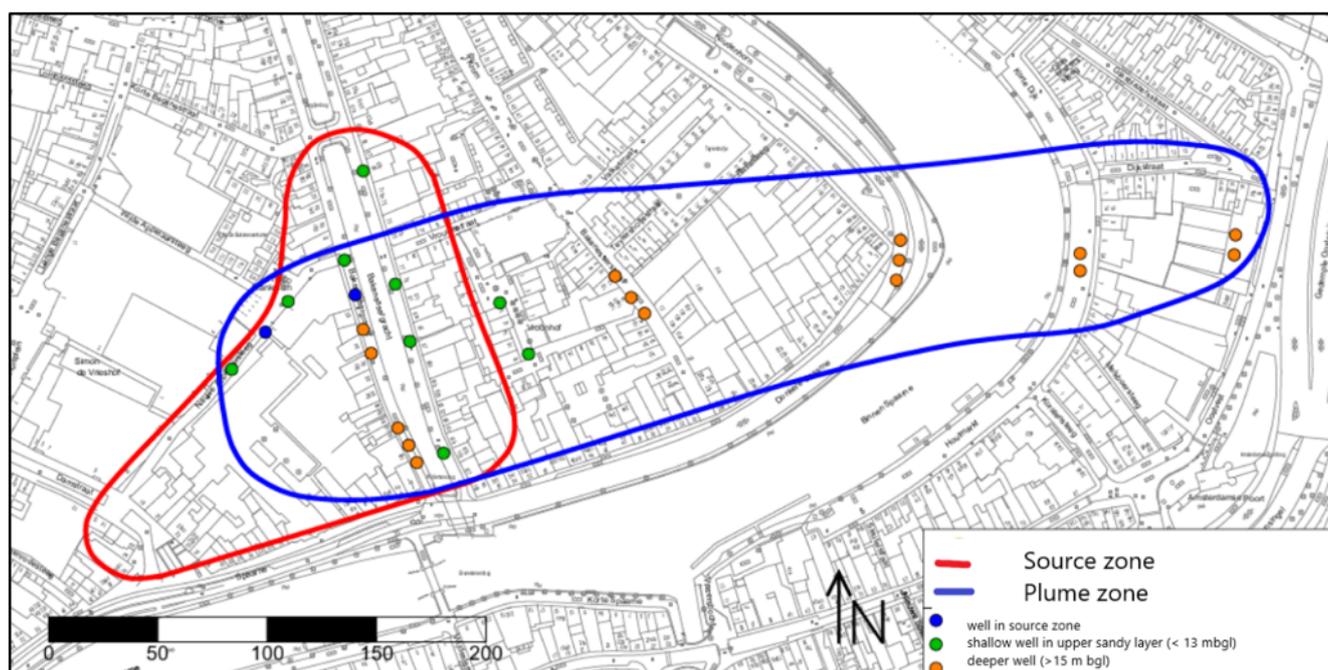

Figure 1: Map of the studied site with indication of the contamination.

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The hydrogeology of the site is characterised by a phreatic layer (0-3 m bgl), a fine beach sand layer (3-13 m bgl), underlain by a peat layer that separates this sandy layer from a first water carrying aquifer (> 14 m bgl). The site is well studied and more than 100 monitoring wells are available, in all geological layers, in the source zone as well as the plume zone.

The purpose of this research is to determine the spreading risk of the residual contamination in soil and groundwater, and to carry out the first monitoring of the water flux and mass flux in the groundwater.

The specific purpose of the iFLUX study is to:
- gain a quicker insight into the behaviour of the contamination in the plume, so that the stable end situation can be demonstrated earlier (if possible);
- find out earlier whether active remediation is still required in the plume; and
- verify the location of the planned deep monitoring wells in the eastern edge of the plume.

3. Materials and Methods

3.1 Mass flux theory
A contaminant mass flux can be defined as the total amount of contaminant, expressed as mass, passing per unit time per unit area through a well-defined control plane that is orthogonal to the mean groundwater flow direction (Bear, 1988; Bear and Verruijt, 1998; Basmadijan, 2004; Newman et al., 2005).

$$J_c = C.q_0 = \frac{m}{A.t} \qquad \text{(Eq. 3.1)}$$

where J_c is the contaminant mass flux [g/m^2/ day], C is the mean concentration of the contaminant in the groundwater [g/m^3], q_0 is the Darcy groundwater flux [m^3/m^2/day], m is the mass of contaminant [g], A is the area of a well-defined control plane, orthogonal to the groundwater flow direction [m^2] and t is the time [day].

An iFLUX sampler determines local contaminant mass and Darcy water fluxes, bounded by the length (b) and diameter (2r) of the cartridge. An iFLUX sampler, installed along a control plane and exposed to a contaminated groundwater flux, will adsorb contaminants from the groundwater while tracer elutes from the sorbent. If an irreversible complete contaminant sorption on the activated carbon is assumed, i.e. for high contaminant-sorbent retardation factors and/or short exposure periods, the contaminant mass flux (J_c) can be calculated as (Hatfield et al., 2004):

$$J_c = \frac{m_c}{2.\alpha.r.b.t} \qquad \text{(Eq. 3.2)}$$

where m_c is the mass of contaminant sorbed by the cartridge sorbent [g], α is the convergence or divergence of flow around the cartridge [-], r is the radius of the cartridge cylinder [m], b is the length of the sorbent matrix or the vertical thickness of the aquifer interval sampled [m] and t is the sampling duration [day].

The Darcy water flux (q_0) through the aquifer can be determined by:

$$q_0 = \frac{1.67.r.R_d.(1 - \Omega_R)}{\alpha.t} \qquad \text{(Eq. 3.3)}$$

where R_d is the retardation coefficient of the resident tracer on the

sorbent [-] and Ω_R is the relative mass of the resident tracer remaining in the PFM sorbent at the particular well depth [-]. More details are provided in Hatfield et al. (2004).

Consequently, flux averaged concentrations (C_J) can be calculated based on the measured contaminant and water fluxes:

$$C_J = \frac{J_c}{q_0} \qquad \text{(Eq. 3.4)}$$

The streamlines around the iFLUX sampler will deviate because of the higher permeability of the cartridge relative to the permeability of the aquifer. This also applies for the streamlines around the monitoring well and the gravel filter around the well filter (Basu et al., 2006; Börke, 2007; Verreydt et al., 2014). The water flux (q) through the iFLUX cartridge is directly proportional to the water flux (q_0) in the aquifer. This can be expressed in:

$$q = \alpha.q_0 \qquad \text{(Eq. 3.5)}$$

where α is the convergence or divergence of the groundwater flow in the vicinity of a monitoring well or passive sampler.

α can be calculated from the potential theory (Drost et al., 1968; Klammler et al., 2007) or simulated through Computational Fluid Dynamics (CFD), based on the hydraulic conductivities of the aquifer, the gravel filter surrounding the monitoring well, the well filter screen and the iFLUX cartridge. These hydraulic conductivities can be determined in the lab. The potential theory supposes a constant α factor and horizontal streamlines through the monitoring well and the iFLUX cartridge. Vertical short circuit currents may have a significant influence on the convergence/divergence of the streamlines.

3.2 iFLUX sampler characteristics
The iFLUX sampler is a passive sampler (Verreydt et al., 2010) that provides simultaneous in situ point determinations of a time-averaged target compound mass flux, J_c, and water flux, q_0. The sampler can be installed in a monitoring well or directly driven into the aquifer where it intercepts the groundwater flow and captures the compounds of interest. The iFLUX sampler is a further development of the passive flux meter (PFM) (Annable et al., 2005; Verreydt et al., 2012).

Table 1: iFLUX sampler characteristics.

| Characteristic	Parameter	Value/description
Dimensions	Length of sampler	33 cm
Cartridges	amount length diameter	2 14 cm 28 - 130 mm
Material	inner tube fixing rod and cable outer mesh	polypropylene stainless steel 100% polypropylene
Sorbent	material mesh size hydraulic conductivity tracers	silver impregnated activated carbon, nonionic resin 5*30 0,00386 m/s methanol, ethanol, 2-propanol, tert. butanol and 2,4-dimethyl-3-pentanol

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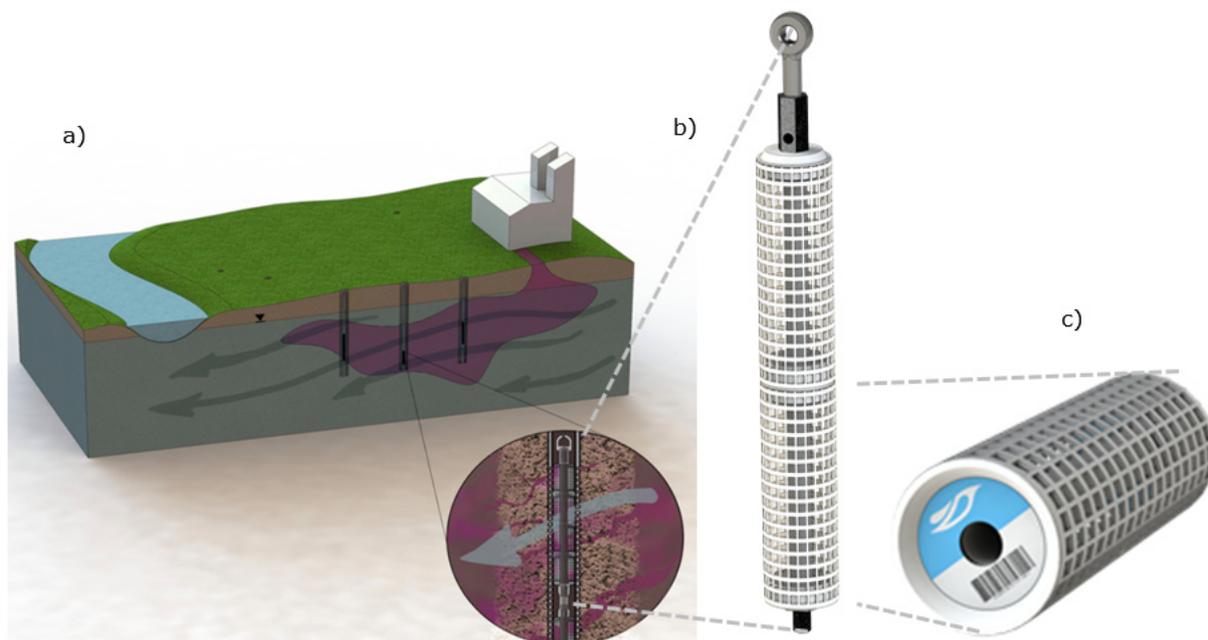
Figure 2: iFLUX sampler, a) field concept, b) sampler chain, c) sampler cartridge.

The sampler consists of permeable cartridges which are each packed with a specific sorbent matrix (Verreydt *et al.*, 2017). The sorbent matrix of the water flux cartridge is impregnated with known amounts of water soluble resident tracers. These tracers are leached from the matrix at rates proportional to the groundwater flux. The measurements of the contaminants and the remaining resident tracer are used to estimate groundwater and target compound fluxes. Exposure times range from 1 week to 6 months, depending on the expected concentration and groundwater flow velocity.

Six types of cartridges are currently validated: volatile organic compounds, metals & heavy metals, nutrients, 1.4-dioxane, PFAS and water flux.

3.3 Selection of monitoring wells for the iFLUX sampler installation

The monitoring wells for the iFLUX sampler installation were carefully selected to 1) allow an easy installation and retrieval, 2) ensure reliable flux data and 3) provide mapping of a vertical flux differentiation in the source zone and a general downstream flux distribution in the plume zone. The selection criteria for monitoring wells eligible for iFLUX sampler installation are listed in Table 2. Well and aquifer specifications should be known in order to estimate the flow convergence/divergence factor (Eq. 3.5).

26 monitoring wells along several transverse transects down-gradient of the suspected source zone were selected. The selected wells were installed at different times and therefore have different materials and borehole details. The monitoring well details are presented in Table 3.

Table 2: Monitoring well selection criteria.

Type	Parameter	Specifications	Comments
Well specific	internal diameter depth	28-130 mm 1.5-130 m	optimal diameter is 51 mm depends on well filter location, maximum installation depth depends on iFLUX sampler weight
	filter slit	> 0.3 mm	filter permeability preferably > 6x aquifer permeability
	gravel filter	gravel permeability ≥ aquifer permeability filter thickness < 1/8 well diameter	flow bypass through the gravel filter has to be taken into account
	well head	undamaged, straight	iFLUX sampler needs to slide straight into well
	installation date	recent	clogging and biofouling will influence the flux measurement
Site specific	location	source/plume one well/several wells along control plane	exact location/selection of wells is based on existing traditional groundwater sampling data

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Table 3: Monitoring well details. For each well the slit size was 0.3 mm and the filter grain size was 0.6/1.2 mm.

Well ID	Location	Diameter ID/OD (mm)	Screen interval (m bgs)
603	Source	25/32	9.9 - 12
619	Source	25/32	10 - 12
622	Source	25/32	11 - 13
701	Source	51/63	1 - 3
701	Source	51/63	6 - 8
A11	Source	25/32	11 - 13
PB13	Source	25/32	0.6 - 1.6
BC06-1	Source	25/32	10 - 12
BC06-2	Source	25/32	16 - 18
BC06-3	Source	41/50	28 - 30
BC06-4	Source	41/50	53 - 55
BC11-2	Plume	25/32	16 - 18
BC11-3	Plume	41/50	26 - 28
BC12	Plume	25/32	16 - 18
BC13	Plume	25/32	16 - 18
BC24-2	Plume	41/50	18 - 20
BC24-3	Plume	41/50	28 - 30
BC26-3	Plume	41/50	48 - 50
BC27-1	Plume edge	25/32	28 - 30
BC27-2	Plume edge	25/32	48 - 50
BC52-1	Source	25/32	10 - 12
BC52-2	Source	25/32	28 - 30
BC50	Source	25/32	12 - 14
BC24-4	Plume	41/50	53 - 55
BC26-2	Plume	41/50	18 - 20

3.4 iFLUX application and handling

The iFLUX cartridges (VOC and water flux) were constructed in the lab and transported to the field. During construction, a sample of each sorbent matrix was collected for the analysis of the initial tracer/blank concentrations.

One cartridge blank of each type was also installed in a monitoring well and immediately retrieved in order to map the installation/retrieval effect on the flux measurements. VOC and water flux cartridges were sometimes combined on sampler rods to obtain both water flux and mass flux information. The completed iFLUX sampler was then inserted into the well down to the desired screen interval (Fig. 3). Every iFLUX sampler was attached to an individual stainless steel cable.

After a specified period of exposure to groundwater flow, the iFLUX samplers were retrieved. The iFLUX samplers in the source zone, including the water flux cartridges in the plume, were exposed for 25-30 days while the remaining samplers with VOC cartridges in the plume were exposed to groundwater flow for 9 weeks 55 days. Subsequently, the cartridge sorbent was carefully extracted to quantify the mass of all intercepted contaminants and the residual masses of all resident tracers. The contaminant masses are used to calculate cumulative time-averaged contaminant mass fluxes, while residual resident tracer masses are used to calculate cumulative time-averaged groundwater fluxes (Hatfield *et al.*, 2004).

3.5 Sorbent analysis

The extraction of the sorbents was performed in the laboratories of SGS. Analysis is performed with a Gas Chromatograph equipped with an automated headspace injection and a mass spectrometer (MS). Measurement uncertainties as determined in the laboratory are 31% for PCE, 27% for TCE, 22% for DCE, 41% for VC and 6.5% for the selected alcohol tracers. More analytical details are provided in Annable *et al.* (2005).

4. Results and Discussion

Tables 4 and 5 show the results of the water and mass flux measurements as well as the direction measurements. The measured flux data is also indicated on maps shown in Figure 4a-d.

Table 4: Overview of water flux data and flow directions. Wells were installed on 8/8/2019 and retrieved 26 days later on 3/9/2019.

Well ID	Cartridge	Depth (m-mv)	Water flux (cm³/cm²/d)	Flow direction (°vs N)
701	W0357	2.12	7	50
702	W0356	7.16	19	320
BC06-3	W0358	28.64	14	120
BC24-2	W0359	19.08	9	80

Figure 3: iFLUX application in the field a) iFLUX sampler with 2 cartridges, b) VOC cartridge on sampler that slides in monitoring well, c) iFLUX cartridges in their packaging bags.

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Table 5: Overview of mass flux data.

Well ID	Cartridge	Installation	Retrieval	Days	Depth (m-mv)	PCE *	TCE *	1,2DCE *	VC *	VOCl sum*
603	O0314	03-09-19	03-10-19	30	10.9	0.57	3200	4534	50	7785
622	O0325	08-08-19	03-09-19	25	11.17	<0.19	<0.19	373	110	483
701	O0302	08-08-19	03-09-19	26	1.98	<0.3	<0.3	<0.6	<0.3	<1.5
702	O0303	08-08-19	03-09-19	26	7.02	<0.3	<0.3	0.45	<0.3	0.45
A11	O0313	08-08-19	03-09-19	26	11.94	<0.19	<0.19	6.7	0.53	7.2
PB13	O0324	08-08-19	03-09-19	26	1.13	<0.19	6.8	10	0.45	17
BC06-1	O0322	08-08-19	03-09-19	26	11.03	<0.19	<0.19	2310	130	2440
BC06-2	O0326	08-08-19	03-09-19	26	16.99	<0.19	<0.19	1510	66	1576
BC06-3	O0310	08-08-19	03-09-19	26	28.5	<0.23	<0.23	844	46	890
BC06-4	O0307	08-08-19	05-09-19	28	52.45	<0.22	<0.22	1083	190	1273
BC11-2	O0318	08-08-19	03-10-19	55	17.08	<0.087	0.87	0.54	0.16	1.6
BC12	O0317	08-08-19	03-10-19	55	17	<0.087	0.79	0.73	0.57	2.1
BC13	O0327	08-08-19	03-10-19	55	16.94	<0.087	8.6	6.5	0.18	15
BC24-2	O0304	08-08-19	03-09-19	26	18.94	<0.23	<0.23	2	18	20
BC24-3	O0306	08-08-19	03-10-19	55	28.94	<0.11	1.8	2.8	2.8	7.4
BC24-3	O0305	08-08-19	03-09-19	26	29.08	<0.23	<0.23	1.4	1.8	3.2
BC27-1	O0321	03-09-19	29-10-19	55	29	<0.087	<0.087	0.96	2.5	3.5
BC27-2	O0316	03-09-19	29-10-19	55	49	<0.087	<0.087	1.9	4.7	6.6
BC52-2	O0315	08-08-19	03-09-19	26	28.96	<0.19	<0.19	128	130	258
BC50	O0319	08-08-19	03-09-19	26	12.6	<0.19	<0.19	0.75	<0.19	0.75

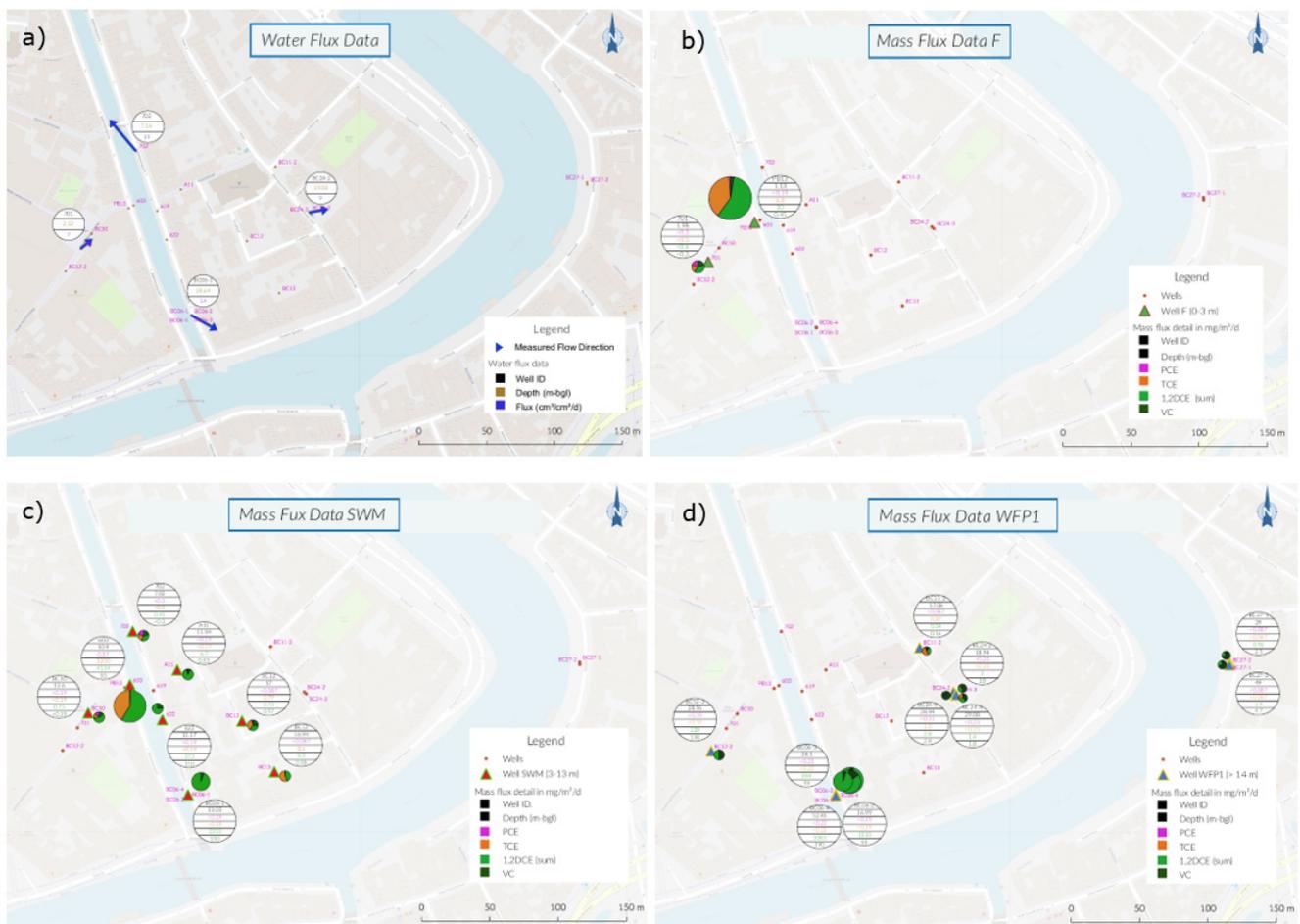*Mass flux in mg/m²/day, no flow field distortion α has been taken into account.

Figure 4: Flux data maps: a) water flux data, b) mass flux data: Phreatic layer F, c) mass flux data: Fine beach sand, SWP and d) mass flux data 1st water carrying aquifer WVP1.

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The water and mass flux results are described below by depth and by location:

- Phreatic layer (F, 0-3 m-mv)
In this phreatic layer (PB13 and 701), only mass fluxes were detected in PB13 for TCE, DCE and VC. Measured water fluxes are about 7 cm³/cm²/day.

- Fine beach sand layer (SWP, 3-13 m-mv)
The highest water flux is measured at 7.2 m-mv in the SWP with a value of 19 cm³/cm²/day in monitoring well 702. The measurements show that the groundwater flow is NNW (angle from 320 ° to the North). In the SWP, upstream (BC50) and at the source (603, 622, 702 and BC06-1), the highest mass fluxes were measured in monitoring well 603 for PCE, TCE and DCE at a depth of 10.9 m-mv. In monitoring well BC06-1, especially high mass fluxes were measured for DCE and the highest mass flux for VC at 11m-mv. In monitoring well 622, high VC mass fluxes were also measured at 11.2 m-mv. In monitoring wells BC50 and 702, the lowest mass fluxes were measured at 12.6 and 7 m-mv, respectively. The results are below or just above the detection limit. In the SWP at the plume (A11, BC12 and BC13), the highest mass fluxes were measured in monitoring well BC13 at a depth of 16.9 m-mv. The mass fluxes here are considerably lower than in the source zone.

- 1st water carrying aquifer (WVP1,> 14 m-mv)
The second highest water flux was measured at 28.6 m-mv in WVP1 with a value of 14 cm³/cm²/day in monitoring well BC06-3. The measurements show that the groundwater flow is oriented SO (angle of 120 ° to the North). In the WVP1 at the source (BC06-2, BC06-3, BC06-4 and BC52-2) for DCE generally lower mass fluxes were measured compared to the SWP. The highest mass fluxes with DCE were measured in BC06-2, BC06-4 and BC06-3 at depths of 17, 52.5 and 28.5 m-mv, respectively.

5.   First Conclusions and Further Perspectives

A first mass flux characterisation of the plume has been successfully performed with the novel iFLUX passive flux samplers. The samplers are proven to be very practical and accurate tools to determine mass fluxes rather than estimate them based on snapshot concentration data that fluctuate in time.

Since this campaign is a first measurement of groundwater and mass fluxes, it is not yet possible to draw conclusions about the evolution of concentrations in the source and the plume. At least a second measurement will have to be carried out for this, as foreseen in the action plan for the flux measurements. The fluxes in the selected monitoring wells will be determined again within 3 years:
1: monitoring active remediation and decreasing flux: 3, 5, 10 years after remediation started.
2: monitoring plume and stable end situation: 10, 20 and 30 years after remediation started.

However, based on the information of this flux campaign, together with all time series of available traditional concentration data, source strength functions (SSF) are currently being determined (Brooks et al., 2008, 2018). This will allow us to predict the behaviour of the plume and therefore react much earlier in time. Whether a stable situation will be reached in the near future, whether remedial actions are still required to prevent from further spreading. It is all about getting a faster insight and deciding earlier on measures and actions.

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