Water-Quality Surveillance of Swiss Rivers

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Abstract. Water-quality surveillance is essential for the detection of anthropogenic impacts on rivers. The surveillance strategy designed by the EAWAG combines long-term, continuous monitoring necessary for assessing the success of measures implemented to fight pollution with short, intensive field and laboratory studies to elucidate element transformations and transport processes. Emphasis is put on sound methods of sampling and sample processing which are paramount for a clear interpretation of river quality data. Results from process-oriented case studies show how a combination of different methods of sampling and analysis brought new insights into phosphorus transport pathways and on the availability of particle-bound phosphate for phytoplankton.

1. Protection of a Threatened Resource

Some consider rivers as mere drainage channels that should be kept under control within artificial banks, be reshaped to efficiently drain the surrounding basin, and readily wash away whatever is released into them. Few realize the links that connect river ecosystems to groundwater habitats, to the catchment, and the role that rivers play within the wider landscape.

Stream water quality is closely related to human health. Globally, rivers gain progressively in importance as drinking-water supplies while groundwater resources become progressively exhausted. In Switzerland, many water-supply plants utilize stream water to recharge aquifers. Beside human health, stream water quality is a value per se which ensures the survival of aquatic organisms and the persistence of natural ecosystems.

Research at the EAWAG addresses the conflicting exploitation of stream water by investigating the impact of urbanization, industrial and agricultural activities, wastewater treatment, and the effects of natural habitats degradation on water quality. In this context, chemical water-quality surveillance is of primary importance; its role can be resumed in four points:

1. detect the presence of contaminants,
2. identify causes of water pollution,
3. evaluate the effect of measures taken to fight it,
4. gain insight into the processes involved in nutrient transport and the potential impact on aquatic organisms.

The strategy implemented at the EAWAG consists in a two-pronged approach: 1) the long-term monitoring of key parameters at selected sites distributed across Switzerland, 2) short-term, intensive, process-oriented field and laboratory studies.

The work presented here is based on results gained by the long-term national river monitoring and survey programme NADUF, and on process-oriented case studies carried out in the Kleine Aa, a first-order tributary of Lake Sempach.

Attention is focused primarily onto nutrient transport, in particular phosphorus (P), which has represented, for many years, a primary concern for national scale pollution control programmes [1]. Studies addressing chemical monitoring of rivers that are not reported here can be found in [2–6].

1.1. Water Quality in Swiss River Basins

Stream water originates from a variety of catchment sources: groundwater exfiltration, springs, and lake outflows. Wastewater inputs together with urban and agricultural runoffs contribute discontinuously but may have an important impact on water quality. Globally, stream water composition results from chemical reactions and biological and physical processes taking place in the atmosphere, in the catchment, and within the riverbed. Rock weathering, erosion, and sediment resuspension are of natural origin. The main anthropogenic impacts are due to:

- alterations of natural discharge patterns (damming, inter-basin transfer),
- increased erosion,
- inputs of nutrients and organic matter which accelerate biological processes and may cause oxygen deficit,
- releases of nondegradable xenobiotic compounds which may be detrimental to stream organisms.

Notwithstanding the high population densities, in comparison to other regions of Europe, Swiss river basins are only moderately polluted. Most Swiss rivers derive from pristine, high altitude springs and exhibit a large runoff/precipitation ratio. In large Swiss rivers ca. two thirds of the average annual precipitation is found in the runoff (ca. 1000 mm yr\(^{-1}\)). In contrast, the average runoff of other large European rivers is only ca. 300 mm yr\(^{-1}\).

Pollution control at point sources is well implemented. The Swiss manufacturing industry is highly developed and its pollution impact is lower than in other countries. In addition, 95% of the population and all industries are served with at least mechanical and biological wastewater treatment, and 75% of all wastewater is chemically treated for phosphorus removal. In addition to ‘end-of-pipe’ measures, the use of potential hazardous substances such as PCBs, Hg, and Cd has been restricted, and polyphosphates are banned in laundry detergents since 1986.

Improved phosphorus elimination in wastewater treatment plants is responsible for additional long-term loading abatement in the main rivers. With these combined measures Switzerland has met the P-loading requirements prescribed by the North Sea Conference aiming at a reduction of nutrient discharge into the endangered sea. More needs to be done to reduce nitrogen loading.

2. Methodological Background to Water-Quality Surveillance

From the planning to the implementation of a sampling programme and to the data interpretation step, chemical monitoring has to take account of the dynamic nature of the composition of stream water. Several problems have to be addressed:
1) Time resolution: changes in concentration occur due to storms, seasonal effects, and variable loads from point sources.

2) Dynamic spatial inhomogeneities within the river caused by incomplete mixing.

3) Sample instability due to chemical, biological, and physical processes (transformation, adsorption/desorption).

The Table summarizes the limits imposed by sampling frequency and mode on data interpretation. In some cases, continuous monitoring may be necessary to provide the time resolution required to assess the dynamics of inputs and transformations. Since, for many parameters, this is hard to achieve, the time schedule of monitoring programmes is determined by an optimized allocation of resources in respect to specific targets.

Time-proportional as well as discharge-proportional sampling involves the storage and eventual mixing of the samples collected. Such strategy is inadequate for unstable species for which field on-line analysis is the only option. The superior accuracy characterizing automated on-line monitoring may be counteracted by the time required for its setup. To ensure a reliable and still not an overly labor-intensive on-line monitoring, the following conditions must be met:

- automated sample collection and processing,
- safe, field-based, automatic storage of analog signals produced by electrodes, photometers, chromatographs, etc.,
- autocalibration at programmable intervals and regular checks of system performance.

The scope of on-line monitoring is limited by the number of parameters that can be analyzed at the same time; often the intensive monitoring of a single parameter cannot fully describe all processes involved in the transport and potential impact of a given element on aquatic biota. For example, to obtain information about the toxicity of NH₃ to fish, NH₃ concentrations have to be computed from the sum of NH₄⁺ plus NH₃, temperature, and pH.

### Table. Sampling Strategy and Data Interpretation

<table>
<thead>
<tr>
<th>Sampling strategy</th>
<th>Aim</th>
<th>Validity</th>
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<tbody>
<tr>
<td>Point sampling combined with continuous discharge measurement</td>
<td>to establish average Q/c relationships</td>
<td>valid for the gross estimate of yearly loads</td>
</tr>
<tr>
<td>Continuous sampling:</td>
<td></td>
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<tr>
<td>(A) time-integrated</td>
<td>(A) to estimate time-averaged water quality</td>
<td>(A) valid for constant discharges</td>
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<td>(B) discharge-proportional</td>
<td>(B) to quantitatively assess average water quality and yearly loads</td>
<td>(B) valid for variable discharges</td>
</tr>
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<td>Continuous on-line measurements</td>
<td>realistic pollution assessment including extreme events</td>
<td>valid for the description of dynamic processes</td>
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<td>Storm event sampling</td>
<td>assess suspended sediment transport</td>
<td>valid for full element transport budgets</td>
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Fig. 1. Evolution of soluble reactive phosphate in the Rhine River at Basel from 1985 to 1996

2.1. Analytical Aspects

Analytical requirements often demand special sample treatment to be carried out in the field immediately after collection (filtration, fixation, immediate storage at low temperatures). In some cases, samples have to be processed on-site, in situ or be analyzed on-line. Each of these techniques is characterized by its own time and space resolution.

Physical and chemical sensors are the techniques of choice for on-line measurements; chromatography is also a potential technique. For low concentrations and in presence of a complex matrix, continuous flow photometry is the commonest option. Air-segmented continuous flow and flow-injection analysis are well established while other techniques such as portable continuous loop analyzers and several other fluid handling systems using precision step motors to drive syringes instead of peristaltic pumps are at the experimental stage. The analytical group of the biogeochemistry department at EAWAG is actively involved in the development of accurate field monitoring devices.

3. The NADUF Monitoring Programme Verifies the Effectiveness of Water-Pollution Control Measures

The Swiss national long-term monitoring programme (NADUF) was established in 1972 as a cooperative project among the Swiss National Hydrological and Geological Survey (LHG), the Swiss Agency for the Environment, Forests and Landscape (BUWAL), and the EAWAG. Its objective is the monitoring of selected chemical and physical parameters in the main Swiss rivers. The data are utilized to investigate processes responsible for water quality and for the success of pollution-abatement programmes.

The national monitoring grid consists of 17 stations distributed all over Switzerland. Discharge-proportional sampling is carried out by means of discharge-integrating automatic samplers. Composite fortnightly samples are collected, stored at 4°C, and analyzed at the EAWAG laboratories. The monitored parameters include dissolved species of: Ca²⁺, Mg²⁺, total alkalinity, Na⁺, K⁺, H₂SiO₄, SO₄²⁻, Cl⁻, NO₃⁻, total N, SRP, and DOC. Suspended particulate matter is analyzed for dry weight, total P, and POC. Electrical conductivity, pH, water temperature, and dissolved oxygen are measured on-line by means of sensors permanently deployed in the field. At some stations, the programme also includes the monitoring of...
NO$_3^-$, NH$_4^+$, Zn, Pb, Cu, Hg, EDTA, NTA, and various detergent additives on a non-
continuous basis. Reports are published yearly in the Swiss Hydrological Year-
book and discussed in scientific articles [7–9].

The effectiveness of the NADUF pro-
gramme is well illustrated by Fig. 1 show-
ing the decrease in phosphate concentration which followed the 1986 ban of phos-
phorus in detergents. A discontinuous sam-
pling programme would have not suc-
cceeded in demonstrating the phosphorus-
loading abatement as it would have not been able to distinguish seasonal from
long-term trends. Seasonal fluctuations are domi-
inated by the summer concentration decrease which is related to the high-
summer discharges (dilution effect) and the summer P retention by terrestrial and
aquatic vegetation which implies also a
higher efficiency in sewage treatment.
Periods preceding the ban are character-
ized by huge variations in P concentration
between summer and winter; such stark
seasonal changes are much attenuated
in the later years.

The decreasing trend in P concentra-
tion was not accompanied by a decrease in
nitrogen. Here again, the availability of
long-term, continuous monitoring data is
a prerequisite for following the evolution
of nitrogen transport. In Fig. 2, annual
nitrate loads obtained by continuous mea-
surements are ordered according to years
with similar discharges to reveal overall
trends that would otherwise be masked by
dilution effects. Presented in this way, the
data for the river Aare suggest a steady
increase in nitrogen transport from the late
seventies to the late eighties. Whether the
observed leveling off, observed in the 90s, is
due to changes in agricultural fertilizer
applications or to special climatic and
flow conditions, remains still an open ques-
tion.

While nutrient loads are being reduced,
new pollutants such as the complexing
agents NTA and EDTA gained impor-
tance at a national scale. Nitrilotriaceta-
te (NTA) is still partly replacing the P build-
er in detergents while ethylenediaminetet-
raceta (EDTA) is used in the photo-
graphic industry, as a conserving agent,
and for many other purposes. Both com-
plexing agents dissolve readily in water and only adsorb weakly on natural parti-
cles. 90% of the NTA is degraded in waste-
water treatment plants, and degradation
continues in natural waters [10]. EDTA is,
however, largely recalcitrant to biodegra-
dation. As a consequence, load and con-
centration of EDTA exceed those of NTA
although the input of the latter is much

**Fig. 2. Evolution of the yearly nitrate load in the Aare River at Brugg from 1975 to 1996**

**Fig. 3. Water dis-
charge, phosphate, ammonium, and ni-
trate concentrations in the Kleine Aa after
a rain storm in May 1993**
higher. NADUF results confirmed that during recent years the loads of EDTA and NTA showed decreasing trends.

4. From Monitoring via Process-Oriented Field Studies to New Conceptual Insights

Already in 1972, Gächter and Furrer [11] recognized that improved wastewater treatment and the banning of polyphosphates in detergents may not be sufficient to meet the goal of bringing Swiss lakes to a mesotrophic state. At that time, estimates for P losses from cultivated soils in the Swiss lowland were 35 kg km⁻² yr⁻¹. According to recent investigations carried out in the Lake Sempach catchment area, current P losses are as high as 150 kg km⁻² yr⁻¹. This value exceeds two- to threefold the estimated load beyond which the lake becomes eutrophic. The main reason for this increase is well known: Due to excessive manure application, the P content of the soil increased by ca. 2500 kg km⁻² yr⁻¹ [12]. As a consequence of this, also the P loss to surface waters has increased during the last decades.

Most studies dealing with P losses from soils to lake tributaries concentrate on erosion and surface runoff. Leaching is mostly considered to be of minor importance [13–15]. This view is supported by the high sorption affinity of SRP (soluble reactive phosphate) to many soil minerals resulting in strongly elevated P concentrations in the fertilized top-soil but leaving deeper layers of the soil profile nearly unaffected. As a consequence, P concentrations in drainage waters are generally much lower than in surface runoff [16].

The Kleine Aa stream drains a subcatchment (6.9 km²) at the northeastern part of Lake Sempach. A large part of the basin (5.4 km²) consists of grassland managed mainly for cattle husbandry and pig production. The grassland is mown up to seven times during the growing season. Liquid manure is applied as frequently, resulting in a total load of ca. 4700 kg P km⁻² yr⁻¹. Ca. 40% of the catchment area is artificially drained, and total losses of SRP into the river yield 115 kg km⁻² yr⁻¹ [6]. These estimates are based on:

1) composite samples taken over 24 h every 13 days,
2) concentration/discharge relationships derived from these samples, and
3) continuous discharge monitoring.

A positive relationship between the SRP concentration and water discharge seemed to support the view that overland runoff was mainly responsible for increased P concentrations at high discharge. However, results obtained from on-line monitoring (SRP, nitrate, and ammonia every 30 min over one year) revealed that SRP concentrations nearly always peaked after the water discharge maximum, regardless if overland runoff occurred, and remained elevated until base flow was achieved again (Fig. 3). NH₄ Concentrations, instead, tended to peak on the rising limb of the hydrograph, whereas nitrate concentrations decreased whenever the water discharge increased. Rainwater had higher NH₄ but lower NO₃ and about equal SRP concentrations as stream water at base flow. Therefore, rainwater reaching the Kleine Aa from impermeable surfaces like roofs, streets, parking areas was responsible for the observed changes in NH₄ and NO₃ concentrations during rain events [6]. Because surface runoff would cease shortly after the end of precipitation, the retarded SRP peaks and the lasting high SRP concentrations suggest that seepage and not overland flow is mainly responsible for the elevated SRP concentrations in the Kleine Aa at high discharge. This conclusion, which disagrees with the widely accepted view that seepage is unimportant for P transport from soils to surface waters, led to a number of process-orientated field studies [17–19]. They demonstrated that a significant fraction of infiltrated rainwater moves along preferential flow paths and eventually is discharged into the river through artificial drainage systems. Water bypassing the soil matrix of the subsoil reaches the river nearly as nutrient-rich as it was when it drained into the macropores close to the soil surface.

This case study shows how, starting from monitoring data, a new hypothesis evolved, which was tested by field experiments and yielded new insights into P transport from soil to surface waters.

4.1. Characterization of Suspended Sediments for an Improved Understanding of Element Transport

Suspended or deposited fine particles represent preferential sites for biogeochemical reactions regulating the dynamic composition of aquatic systems. The last ten years have witnessed an escalating interest in the study of particles in natural waters [20][21].

Suspended sediments (SS) are heterogeneous and unstable components of aquatic systems. Their properties are determined by:
- erosional sources active in the catchment,
- factors affecting accumulation and early diagenesis within the streambed [22],
- aggregation of fine clays and colloids, flocculation and chemical precipitation.

Suspended sediments properties can be resumed only by the determination of a relatively large number of parameters. Among these, concentration (expressed as weight or number of particles per liter), size, shape, volume, surface, density, and elemental composition are all relevant for...
the study of chemical processes. As for many water-quality parameters, also SS characteristics cannot be preserved and should be analyzed in the field and if possible in situ. At present, methods of particle analysis have not been developed to the stage of intensive routine monitoring. At the EAWAG, the Particle Laboratory can rely on several facilities for applied particle analysis. These include single-particle counting, zeta potential analysis, static and dynamic light scattering, BET-specific surface analysis, scanning electron microscopy, and field flow fractionation. Devices for in situ (underwater) particle sizing and counting have been recently developed [23][24]. Fig. 4 shows the evolution of discharge and SS surface during a storm event computed from particle counting and size measurements performed with a single-particle laser counter.

Studies dealing with the physicochemical properties of particles in aquatic ecosystems are concerned with the interrelationship between size, geochemistry, and transport capacity. The analysis of separate particle fractions is a necessary tool for the understanding of element transport and to study the association of various elements with different matrices.

### 4.2. Losses of Particulate P

The transport of most particulate matter in rivers takes place during infrequent periods of high discharge associated with rain events [9][25]. Calculations based on concentration-discharge relationships can estimate yearly loads only with gross approximation since each individual event has its own specific behavior. During rain events, SS characteristics may change by several orders of magnitude within short time. Particle concentration increases during the rising limb of the discharge hydrograph attaining sometimes values of the order of few g/l. Then it decreases rapidly during the receding limb. As expected, elements with high particle affinity (P, C, several metals) show a similar behavior. At high discharge, particle-bound species may exceed the concentration of dissolved species often by more than tenfold. Conversely, under base flow conditions, suspended sediment concentrations may fall below 10 mg/l, and dissolved species become predominant.

A process-oriented study analyzing particle-bound pollutants was recently carried out in the Kleine Aa. The main aims were to estimate the contribution of particulate phosphorus (PP) to the total phosphorus flux, to investigate exchange mechanisms between particulate and soluble phosphorus, and to study relative PP availability by to phytoplankton in Lake Sempach by means of physical (particle size) and chemical (sequential extraction) fractionation techniques applied to suspended sediment.

In the Kleine Aa, the yearly hydraulic load is dominated by storm runoff. During rain events the concentrations of total P and suspended sediments increase drastically, however, the P content of SS tends to decrease (Fig. 5). This pattern is not unexpected and is generally attributed to flow-related variations in particle size [20]. Large particles transported during high flow are expected to have a lower P content due to their lower specific adsorption surface and to the lesser content of metal oxyhydroxides which exhibit a high affinity for phosphate. This general explanation is somewhat confirmed by:

1. the complex relationship existing between discharge and particle size which are not always positively related [26],
2. the succession, during the high discharge event, of runoffs having different sources in the catchment [27],
3. the fact that the ratio of soluble to particle-bound elements may change due to fast adsorption/desorption reactions [28][29].

Investigations by means of sequential chemical fractionation [30][31] identified several extractable P forms in the suspended sediment. Fig. 6 shows the result of such an extraction carried out during base flow (0.055 m³/s) when particle concentration was extremely low (4 mg/l), P content of suspended sediment was high (3.27 mg PP/g SS), and the P transport flux was dominated by soluble reactive phosphate (44 µg SRP/l, 13 µg PP/l).

Phosphate was measured in the four extracts (NH₄Cl-P, BD-P, NaOH-P, and HCl-P) before and after persulfate digestion. The residual pellet was also digested (K₂S₂O₈-P). The NH₄Cl-P extract is an immediately available, sorption-exchangeable P pool. The BD-P extract, interpreted as reducible metal-bound P, showed the highest P concentrations among the undigested extracts. This fraction is considered bioavailable as it may be released from particles as they approach the anoxic boundary at the sediment/water interface. The NaOH-P extract (humines, polyphos-
phates, and other organic P compounds) had the highest P content among the digested ones. The NaOH-P fraction consists of P that can be released only after bacterial or chemical oxidation [31]. Other particulate P forms contributed little to the overall result of the fractionation. Residual P, a non-extractable, refractory P pool, represented some 12% of the total PP. The result illustrated in Fig. 6 is typical of base flow conditions which occur 80% of the time. When the fractionation is carried out on samples collected during high discharge events, it can be observed that decreases in the BD-P fraction account for a significant part of the decrease in the P content of suspended sediment during the rising limb of the hydrograph when suspended sediment concentrations are highest. This means that the highest proportion of PP transport is characterized by particles having a low content of bioavailable P.

The impact of SS on the concentration of elements in solution remains highly debated. Hydrologists tend to regard stream as conveyor belts transporting minerals and water in a nearly conservative manner. On the other hand, geochemists stress the importance of in-stream processes and rapid exchanges between solids and solution [28]. Work carried out at the EAWAG in the late 80s on the distribution of Pb and Zn between dissolved and particle-bound forms showed that theoretical partition coefficients (soluble species/particle-bound species) for solutions characterized by different particle concentrations can be derived from estimates of element-specific binding capacities obtained from sorption experiments [32]. This model can approximate the effect of suspended solids on solute concentration during storm events [28].

4.3. Processes at the Channel Bed

Biogeochemical processes at the sediment/water interface in rivers are responsible for changing the composition in the overlying water. If the concentration of a pollutant is decreased by such chemical or microbial processes, one speaks of self-purification. In a recent project, the self-purification capacity of the biofilm community has been investigated in the river [33]. It appeared that as fine sediments accumulate during base flow, microorganisms rapidly colonize this nutrient-rich environment, grow, and form a biofilm. The development of biofilm nitrifiers is limited by ammonium concentrations and is dependent on the persistence of base flow. During high discharges accompanied by the scouring of the riverbed by gravel and coarse sediments, the biofilm is wiped out, and no nitrification can be measured.

5. Conclusions

No single general strategy for the successful monitoring of rivers exists. Depending on the aim of the study, different modes of sampling and analysis need to be chosen.

If the aim is just to determine the yearly loads of a poorly reactive species or of an element regardless of its speciation, then point sampling combined with continuous discharge measurements or continuous, discharge-proportional composite sampling may be adequate.

If focus is put on the behavior of different chemical species, then, obviously, total element analysis is not sufficient.

If diurnal changes in concentration or unpredictable short-term changes (e.g., discharge fluctuations) are to be investigated, then sampling and analysis of a larger number of individual samples may be needed. Continuous on-line measurements might be the best method in such cases. It should be emphasized, however, that data quality produced by such automatic techniques is tied to the maintenance of the monitoring system. Signal drifting, filter clogging, bacterial growth on membranes, electrode poisoning, and unpredictable effects such as sudden power failures, call for a very intensive surveillance.

If processes within the river channel such as self-purification are to be elucidated, then the monitoring of the flowing water may give some information, but additional investigations of processes occurring at the riverbed are necessary to fully understand the overall transformations and the mechanisms controlling it.

Advancements in our understanding of nutrient transport derive from the synthesis of results obtained by different approaches. A better identification of transport pathways is a prerequisite for the design of new, more pertinent control measures to limit phosphorus losses to surface waters.

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