Sampling and Partition of Neutral Organic Contaminants in Surface Waters With Regard to Legislation, Environmental Quality and Flux Estimations

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SAMPLING AND PARTITION OF NEUTRAL ORGANIC CONTAMINANTS IN SURFACE WATERS WITH REGARD TO LEGISLATION, ENVIRONMENTAL QUALITY AND FLUX ESTIMATIONS

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The distribution of neutral organic contaminants among the different phases in surface water is predicted from the octanol–water partition coefficient (K_{ow}), resulting in a reasoned sampling approach. Most pitfalls in methodology of sampling and the determination of partition coefficients appear to origin from adsorption. For contaminants with K_{ow} values $<10^4$ environmental quality of surface waters, represented by the truly dissolved contaminants, can be determined by simply sampling the dissolved phase. For more hydrophobic contaminants sampling suspended particulate matter (SPM) is prefered as this method is hardly afflicted by adsorption problems. The contaminants truly dissolved content then can be estimated through the partition coefficient. Results of the SPMs contaminant contents, expressed per weight units organic carbon, allow spatial and temporal comparison to be achieved. Estimating fluxes of contaminants, mainly bound to organic matter (particulate and/or colloidal), should be focused on accurately determining the flux of this organic matter. Application of continuous–flow centrifugation for sampling suspended matter shows many advantages.

INTRODUCTION

Contaminants are sampled and analyzed in water for several reasons. To reduce the contamination level, national and international *legislation* has set limits to admitted concentrations in waste and surface waters. Limit values can vary depending on the use of the water and usually concern the total unfiltered sample which is appropriate to controle waste water and drinking water intake.

For surface waters the legislator should recognize that toxicity, in terms of bioavailability, for most contaminants is influenced by the presence of complexing or adsorbing matter[1–4]. The concentrations in total water samples of contaminants mainly sorbed to suspended matter will be strongly determined by the sampling conditions as the suspended matter content will vary with meteorological and hydrodynamical conditions. This does not imply that the *contamination level* is varying. Therefore, when estimating temporal or spatial differences, results often have to be corrected for the variation in natural parameters in a similar manner to that applied to sediments[5,6]. Such corrections have to be implemented to achieve *environmental quality* criteria for surface waters. For

sediments Di Toro *et at*[4] described the technical basis for setting quality criteria based at equilibrium partitioning. The toxicity of a sediment could be related to the truly dissolved content of a contaminant resulting from partitioning. This truly dissolved concentration is often regarded as the fraction being available to biota and is proportional to the fugacity[4,7]. During equilibrium the fugacity, i.e. a measure for the contamination level, is principally the same for each phase. The relation with fugacity makes the truly dissolved content a key parameter in monitoring the environmental quality of surface waters but for strongly hydrophobic contaminants practical limits do not allow accurate determination and it could be suggested to calculate the truly dissolved content from the particulate matter by *partition coefficients*. This implies that studies aimed at estimating the partition coefficients are strongly related to the determination of environmental quality.

In addition to limiting the contamination level there are also regulations to reduce contaminant *fluxes*. For examples the nations along the river Rhine agreed to reduce the contaminant flux of the river Rhine to the North Sea by at least 50%. To study transport and estimate fluxes, total water samples[8] are analyzed as well as dissolved and particulate fractions separated by centrifugation[9,10]. The contaminants in the dissolved phase behave conservatively while for contaminants adsorbed to suspended matter the transport is highly subject to hydrodynamical conditions. Therefore it is important to distinguish between both phases. For contaminants mainly sorbed to suspended matter only the solid phase is contributing to the flux[11]. However adsorption of contaminants to dissolved colloidal matter enhances the contaminant content in the dissolved phase compared to the content expected from the partition coefficient[12].

In this paper a theoretical model, based on the octanol water partition, is given for the distribution of organic contaminants between the phases present in water with special emphasis on the implications for sampling. The model is applied to the fields of interest: legislation, environmental quality and contaminant fluxes. An overview is given of possible sampling and analytical pitfalls. The methodology related to the determination of partition coefficients and its artifacts are discussed. The theory and practice are combined with considerations for the legislator and the chemist to select the appropriate sampling method. Discussion on environmental quality is based on the equilibrium concept as presented by Di Toro *et al*[4]. An alternative approach in relation to the measurement of contaminant fluxes is suggested.

DISTRIBUTION MODEL

Equilibrium partitioning

In sampling water for organic contaminants it is important to know the distribution of the contaminant in the various phases. At equilibrium the ratio between adsorbed and dissolved is expressed by the water–sediment partition coefficient (Kp): The suspended particulate matter (SPM) is assumed to be of the same composition than sediment particulate matter as it is considered to be non settled sediment.

$$K_P = \frac{C_{SPM}}{C_{DIS}} \tag{1}$$

Where C_{SPM} is the content of a contaminant in SPM and C_{DIS} is the truly dissolved content. The Kp is largely determined by the SPM organic carbon fraction and is therefore transposed to a K_{POC}[4] by dividing it by the organic carbon fraction (f_{oc}) of the SPM (eq 2).

$$K_{OC} = \frac{K_P}{f_{OC}} - \frac{C_{SPM}}{f_{OC} C_{DIS}} = \frac{C_{POC}}{C_{DIS}} \qquad (2)$$

In eq. 2, C_{POC} is the contaminant concentration per weight units of POC, where POC represents the particulate organic carbon. With filtration or centrifugation an operationally defined particulate and dissolved phase will be obtained. Apart from the truly dissolved phase, filtrates and centrifugates will contain small particles, organic colloids and dissolved organic matter referred to as colloidal organic carbon (COC). Similar as for POC the adsorption of contaminants to COC is expressed by the K_{COC}.

$$K_{POC} \cong K_{COC} = \frac{C_{COC}}{C_{DIS}} \qquad (3)$$

Here C_{COC} is the contaminant content per weight unit COC. The K_{POC} and K_{COC} are controlled by the same thermodynamics and proportional to the hydrophobicity of the organic contaminant as reflected by the octanol–water partition coefficient (K_{OW}). These parameters show a strong relation as reported by Karickhoff et al.[13] (log–K_{POC}=logK_{OW}–0.21) and Hassett et al.[14] (logK_{POC}=logK_{OW}–0.317). As in practice the determination of K_{POC} values above 10^5 is hindered by the inability of isolating the truly dissolved phase often resulting in an underestimation of K_{POC}[15,16]. K_{COC} values are reported to be lower[17] as well as equal[18–20] to K_{POC} or K_{OW} values. Considering this, Di Toro et al[4] assumed that $K_{OW} \approx K_{POC} \approx K_{COC}$, reflecting the upperbound values from literature. Therefore, in the model, K_{OW} values should be used to predict the distribution among the phases in the water. Nevertheless, the partitioning coefficients will be indicated by different symbols to distinguish them in the discussion. Where no reliable measured values are available, calculated values from molecular topology[21,22,23] may be applied for the model. In Figure 1, the truly dissolved fraction is plotted against the K_{OW} value for several POC+COC contents.

Although K_{OW} values may be applied for chosing the right sampling approach, accurate K_{POC} and K_{COC} values are crucial with regard to bioavailability and
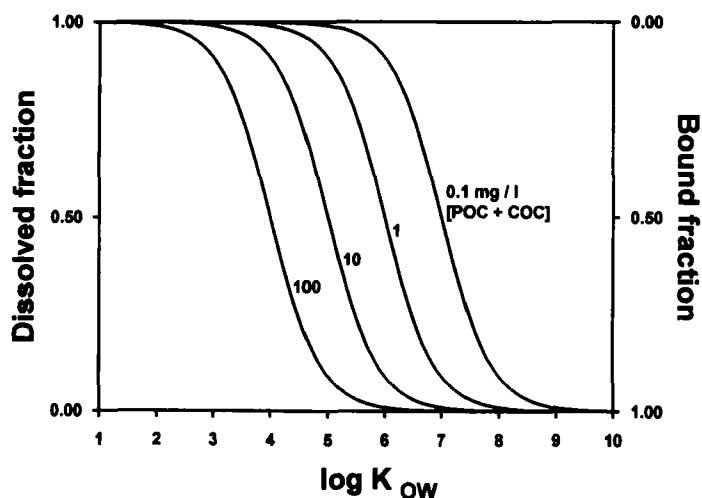

Figure 1 Distribution between truly dissolved (C_{DIS}) and adsorbed fraction in relation with the octanol – water partition coefficient (K_{OW}).

environmental quality. Literature values often suffer from the practical limits of isolating the truly dissolved phase resulting in apparent K_{POC} values. This apparent partition coefficient, K_{APP}, is the ratio of C_{POC} and the operationally defined dissolved content i.e. the sum of C_{DIS} and the COC bound[4,24].

$$K_{APP} = \frac{C_{POC}}{C_{DIS} + C_{COC}[COC]} \tag{4}$$

The previous assumption that K_{POC} is equal to K_{COC} implies that during equilibrium $C_{COC} = C_{POC}$ (eq 2 and 3). After division of numerator and denominator by C_{POC} and substituting C_{DIS}/C_{POC} by $1/K_{POC}$ a relation is obtained in which K_{APP} is depending on the K_{POC} value and the COC content.

$$K_{APP} = \frac{1}{\dfrac{C_{DIS}}{C_{POC}} + [COC]} = \frac{1}{\dfrac{1}{K_{POC}} + [COC]} \tag{5}$$

If the COC content is much lower than $1/K_{POC}$, i.e. K_{POC} is small, the $[COC]$ can be neglected and K_{APP} is equal to K_{POC}. For higher K_{POC} values, the K_{POC} term will diminish and the K_{APP} is inversely related to the COC content and independent of the hydrophobic properties of the contaminant[4,25,26].

$$K_{APP} \approx \frac{1}{[COC]} \tag{6}$$

Plotting the log values of the fractional contents of the three phases against the K_{ow}, Figure 2 is composed. The dotted line represents the operationally defined dissolved content. It is clear that the K_{APP} will be constant for higher K_{ow} values and is only depending on the COC content, and subsequently, the effectness of the separation technique. Therefore, measured K_{POC} values usually show an upper limit of $\approx 10^7$, even if the corresponding K_{ow} is much higher[27]. Next to the operational limitations, the C_{DIS} becomes extremely low for high K_{ow} values which will undoubtedly lead to analytical
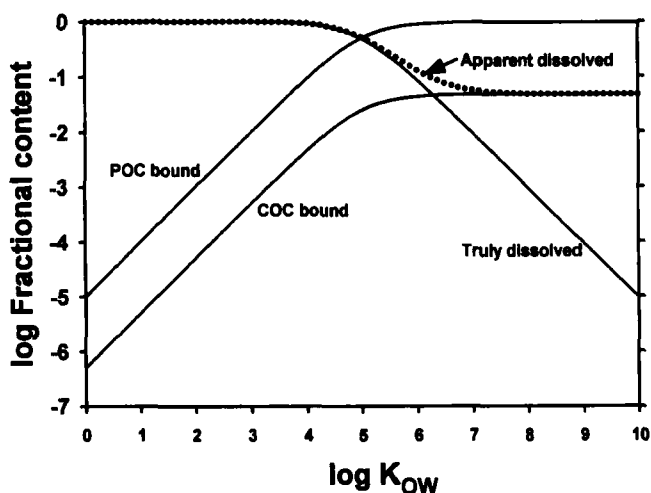
Figure 2   Relations of the fractional contents (log) of the contaminant content in the whole watersample for the three phase in water with the K_{ow} (log). In this example the POC content is 20 mg/L and COC content 0.5 mg/L. The experimentally defined fraction is reflected by the dotted line.
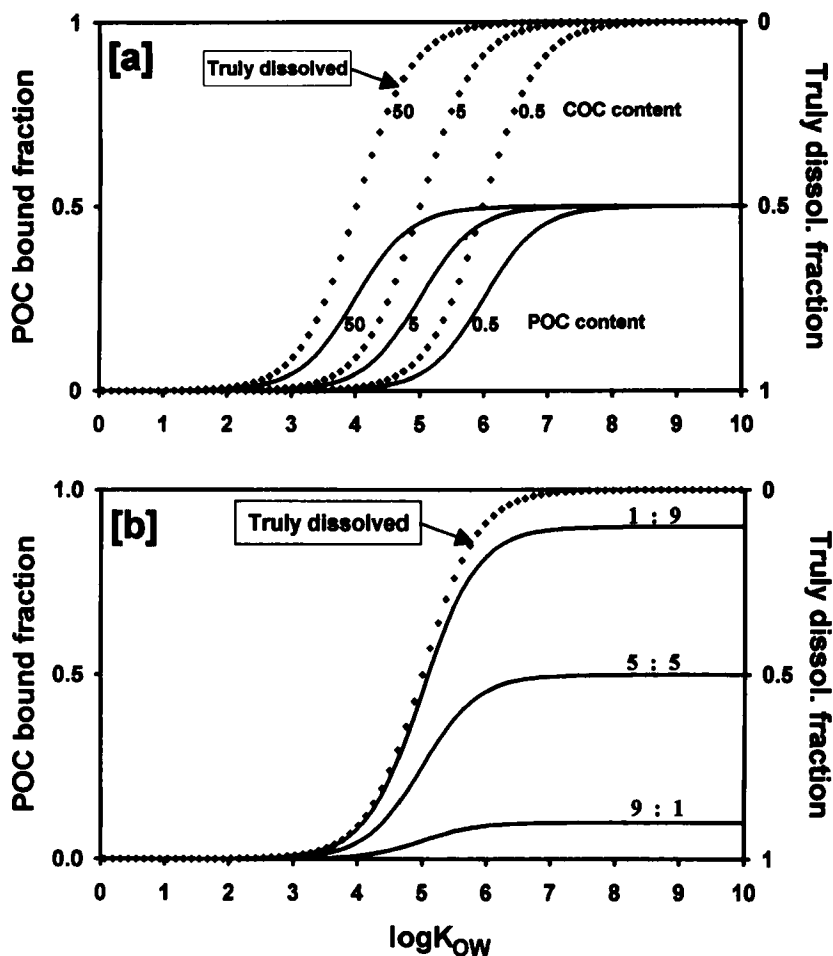
Figure 3 Calculated F_{POC} values in (solid line, left scale) relation with the $\log K_{ow}$ for [a] 3 values of [POC] (0.5, 5, 50 mg/L) and a fixed (1:1) ratio to COC, and [b] a fixed [POC+COC] (10 mg/L) and several COC:POC ratios. The dotted lines represent the truly dissolved fractions and correspond to the right axes.

difficulties. In the discussion several artifacts occurring in the estimation of K_{POC} values will be explained by the model described.

Fluxes

In the determination of fluxes the experimentally dissolved fraction should preferably be defined as the non settling fraction after centrifugation, since this fraction can be assumed to behave conservatively, when the transport of contaminants adsorbed to particulate matter depends strongly on hydrodynamical conditions. Again, three fractions can be recognized in water; F_{POC}, F_{COC} and F_{DIS} respectively representing POC bound, COC bound and truly dissolved.

$$1 = F_{POC} + F_{COC} + F_{DIS} \tag{7}$$

In eq 8 F_{POC} is expressed by the subsequent parameters:

$$F_{POC} = \frac{C_{POC}[POC]}{C_{TOT}} = \frac{C_{POC}[POC]}{C_{POC}[POC] + C_{COC}[COC] + C_{DIS}} \tag{8}$$

After division of both numerator and denominator by $C_{POC}*[POC]$ and assuming that C_{POC} and C_{COC} are equal, the eq. develops into:

$$F_{POC} = \frac{1}{1 + \dfrac{[COC]}{[POC]} + \dfrac{C_{DIS}}{C_{POC}[POC]}} \tag{9}$$

Sustitution of C_{DIS}/C_{POC} by $1/K_{POC}$ results in a relation where F_{POC} depends on the K_{POC} coefficient and the contents of POC and COC.

$$F_{POC} = \frac{1}{1 + \dfrac{[COC]}{[POC]} + \dfrac{1}{K_{POC}[POC]}} \tag{10}$$

From eq. 10 it follows that the POC content determines at which K_{POC} the F_{POC} becomes significant as illustrated in Figure 3a where the F_{POC} is plotted against the K_{ow} for several POC contents maintaining a constant ratio between [POC] and [COC]. The distance between the F_{POC} and F_{DIS} represents the COC bound fraction. Figure 3b demonstrates how for a constant [POC+COC], the ratio between [COC] and [POC] influences the F_{POC}. At high K_{ow} values, when the truly dissolved phase is negligible, the COC bound fraction is independent of the K_{ow} meaning that contaminants quantitatively adsorbed still can be transported like water which is important in estimating fluxes.

EXPERIMENTAL CONSIDERATIONS AND PITFALLS

Sampling

The basis of all environmental studies is sampling, which problems are generally underestimated. Most of the problems that occur are all related to adsorption on sampling tubes, bottles, filters, suspended material and COC. When sampling tubes or equipment are used they must be clean and equilibrated with the sample by pumping an appropriate time and at very high flow rate to create steady state conditions. For pumps (non–lubricated) and tubes only the use of materials like stainless steel, glass, PVDF, teflon or related materials are generally allowed. Experience gained on Dutch sampling vessels has shown that a flow rate of above 1 m³/hr and a linear velocity of more than 1 m/sec in the tubing seems appropriate for dissolved components as well as suspended matter.

Experiments to validate sampling systems are extremely difficult. A basic test is to check for (cross) contamination by comparing most different locations which are simultaneously sampled with plunging bottles. Also analysing a methanol washing after sampling and comparing the amounts found in the methanol with amounts in the pumped

sample provides information if contamination of the system, or through the system, can be expected.

Sample bottles for transport and storing can cause losses through adsorption to the wall which occurs, respectively, from $K_{ow} \approx 10^4$ and $K_{ow} \approx 10^5$ for teflon and glass bottles[28]. Glass bottles are therefore preferred to teflon. Chemists should be aware of this adsorption as it prohibits the rinsing of the sampling bottle in advance of filling as well as subsampling. The bottle and stopper also should be extracted to include the adsorbed fraction. Rinsing and equilibrating the bottle with the sample theoretically allows subsampling but is not recommended as samples, temperature, and distribution change during storage.

Centrifugation is a convenient way to separate the settling particulates from the nonsettling fraction. Using a batch centrifuge the same adsorption problems that pertain to sample bottles will occur. With contaminants that possibly adsorb to the centrifuge tubes it is necessary to equilibrate the tubes with the sample before filling to avoid losses through adsorption. Further, the sample volume obtained by a batch centrifuge will generally not be sufficient for accurate analyses as contaminants susceptible to adsorption usually have low dissolved concentrations.

A continuous–flow centrifuge on the other hand can process an almost unlimited amount of sample and is easily equilibrated. Typical conditions for a continuous–flow centrifuge are a sample flow of 1 m^3 per hour and a gravity of 10000 g[9,11]. Due to the limited residence time in the centrifuge the efficiency is worse than a batch centrifuge. Size and density of the particles strongly determines their retention behaviour. It is clear that a centrifugate contains colloidal organic carbon as well as low density particles. Physically, in the view of transport, material passing the centrifuge behaves like dissolved.

Filtration of water samples is subject to adsorption of the filtermaterial and clogging of the filter by SPM. Quantitative adsorption to membrane filters for the full range of chlorinated biphenyls (CBs)[29] and full adsorption of several pesticides ($K_{ow} > 10^3$) to cellulose nitrate filters, were reported[28]. Inorganic filters like Anapore (Whatman) and precombusted glassfibre filters showed less adsorption of the test compounds. The lower adsorption, but certainly not negligible, was obtained by the glassfibre filters but without a relationship with the K_{ow}. This non-relation was confirmed by adsorption experiments with chlorinated biphenyls[29] and polyaromatic hydrocarbons[30].

All the experiments on filter adsorption were done with organic free water so the compounds may be considered to be truly dissolved and, therefore, readily available for adsorption. In natural water, however, those contaminants are often (partially) bound to the COC[12] which carries them through the filter. In case of high K_{ow} values the COC bound fraction will outnumber the truly dissolved content (see figure 2). The loss through adsorption is then limited to the minor truly dissolved and the extent in which COC is adsorbed by the filter[31].

Filtration using glassfibre filters showed a significant decrease in contaminant throughput as the filtration proceeds due to a decrease of the average pore diameter cause by clogging of the filter[29]. This makes it useless to compare results from filtrates of different locations as the nature and content of SPM and COC influence the effective throughput of COC. Comparison of measurements in filtrates is only possible if it is certain that the contaminant of interest is truly dissolved ($K_{ow} < 10^4$) or when the COC responsible for adsorption is properly defined and whose contribution can be corrected for.

Extraction

The isolation of contaminants from water samples can be hindered by adsorption to bottles, POC and COC. Applying liquid–liquid extraction (LLE), the bottle can easily be extracted using the extraction solvent. Preferably, a water miscible solvent should be used. Hermans *et al*[29] developed a continuous batch extractor which could be placed on the sampling bottle (10 L) extracting the sample and the bottle wall. Bottle rinsing is more difficult when solid phase extraction (SPE) is used. The elution solvent can be used but then it will be diluted with water, hence losing elution poser. The SPE method works well for K_{ow} values above $10^{1.5}$, high enough to support extraction to the solid phase, and K_{ow} up to approximately 10^4, where adsorption to SPM and COC does not yet occur. Above $K_{ow} = 10^4$, the solid phase extraction can be incomplete as contaminants bound to COC are generally not retained by SPE[32,33]. A possible extension of the use of the SPE method upto $K_{ow} \approx 10^5$ is the addition of 20% methanol to the water sample. This increases the solubility[34,35] resulting in an apparent decrease of the K_{ow} by one order of magnitude. Although the break–through volume for SPE decreases also this is not dramatic provided the K_{ow} is still high enough. Next to this the phase–exchange is improved through a much better wettability[30] while the adsorption to the bottle wall is reduced also.

At K_{ow} values above $\approx 10^5$ a major part of the dissolved fraction can be COC bound depending on the COC content. *Contaminants do not desorb from COC instantaneously*[36,37] when the truly dissolved fraction is removed[32], meaning that for LLE the extraction time should exceed the time necessary for complete desorption of the COC bound contaminants. Applying a batch continuous liquid–liquid extractor using hexane extraction, times for chlorinated biphenyls (CBs) of ≈ 30 and ≈ 70 hours were reported for, respectively, glassfibre filtrates and centrifugates[29]. Acidification together with aging reduced the extraction time of centrifugates to 24 hours. The desorption rate shows an inverse relation to the partition coefficient[38]. This indicates that when extracting the whole sample, including SPM, the extraction times will be even higher. Extraction of water with a SPM (unspiked) load of 1 g/L using hexane showed extraction times of approximately 7 days for CBs and polyaromatic hydrocarbons[39]. Considering that the extraction rate, is reflecting the maximum desorption rate the use of SPE should be restricted to contaminants with K_{ow} values $< 10^4$ or $< 10^5$ when a modifier is applied.

COC contents

The dissolved organic carbon (DOC) or total organic carbon (TOC) are often regarded as COC. In experiments comparing filtration and centrifugation the CB153 contents in effluents were found to differ more than a factor 20 because of an expected variation in COC content. However, the measured dissolved organic carbon (Persulphate/UV method)[40] contents did not significantly differ, meaning that the expected relation of DOC and contaminant concentration did not show up[29]. The persulphate/UV oxidation determines only the low molecular weight fraction and perhaps some of the easy oxidized colloidals[41,42]. The low molecular weight material might show some cosolvency[43], but is not capable of adsorbing contaminants[44]. Catalytic oxidation at high temperature[41], the so called TOC analyzer, determines both organic fractions and showed higher[45] or equal[46] results.

Because TOC also includes the low molecular weight fraction this value cannot represent the COC either. The difference between the TOC and DOC content might

represent COC[41,47] but suffers from a high variability and varies for applied methods[45], so the usefulness for correlation with the contaminant content is doubious. A promising method is the application of ultrafiltration to isolate to COC and determine the COC content, as the difference in carbon content of total sample and filtrate[19,44].

Next to developping accurate methods of determining COC, more knowledge on the physical and chemical properties of colloidal matter should be obtained. To apply methods for characterization, often a preconcentration step is required like ultrafiltration[44,48], SPE[49], reversed osmosis[50], etc. Characterization by size exclusion chromatography[51,52], NMR[53], determination of molecular weight[54] and elemental analyses[55] can support a better understanding.

DISCUSSION

Determination of partition coefficients

Partition coefficients are important with regard to bioavailability and establisment of environmental quality criteria. Therefore, accuracy and international agreement should be demonstrated. In the following lines research on the estimation of K_{POC} and K_{COC} is summarized and possible artifacts limiting the application are given. The determination of the C_{DIS}, needed for estimating K_{POC} (eq 2) is the most critical step. Filtration or centrifugation is often applied in spite of the previous described artifacts.

Equilibration of increasing amounts of sediment with water showed increasing COC contents in the dissolved phase[24,56], subsequently resulting in a lower K_{APP} value for higher sediment loads.

From an overview of several samplings, Duinker[57] reported for CBs an almost 100 fold enhancement of the K_p (eq 1) for decreasing SPM contents. While in the examples above, the content in the dissolved phase was increasing with higher SPM contents. Duinker[57] observed rather constant CB contents in the waterphase but the C_{SPM} was increasing tremendously. Small low density particles were considered responsible. However, carefully studying the procedures and results, filter adsorption in addition to an increase of the organic carbon fraction of the lower SPM contents, could have caused adversed results. This is supported by two observations:

(1) The relative enhancement of C_{SPM} was much larger for CB18 and CB52 than for CB180, which can be caused by the much higher K_{OW} of the latter, meaning that CB180 will be mainly bound to COC, carrying it through the filter, while the others are more present in the truly dissolved phase and therefore are available for adsorption.

(2) It is not likely that a two–fold drop in [SPM] shows a more than two–fold increase in C_{SPM}. This would imply that the fine particles would not be present at higher SPM contents.

From the examples give above we learn that, using filtration to determine K_{POC} values, the influence of COC should be expelled and adsorption problems should be controlled. Washing the sediment to remove COC[15] can be an improvement but only extends the measurable range as there is always some residual COC or new COC possibly released from particulate organic matter through breakdown.

The SPE method (K_{POC} and K_{COC}) to isolate C_{DIS} is based on the assumption that the SPE adsorbed fraction represents the truly dissolved fraction, while bound fraction passes through the column[32]. However, when the truly dissolved fraction is very low, the

presence of a small labile COC bound fraction or significant COC adsorption to the SPE column can easily result in an overestimation of the truly dissolved content[58].

Dialyses to isolate the C_{DIS} was successfully applied for COC as well as for POC partition using radiolabelled compounds[32,59]. A disadvantage is that for highly hydrophobic contaminants very high activities have to be used to obtain a measurable activity for the C_{DIS}. Additionally, it should be noticed that using radiolabelled compound for partition studies, underestimation of partition coefficients can occur if a 99.9% pure compound contains 0.1% water soluble radioactive impurities.

Gaspurging has been applied to estimate C_{DIS} starting from the assumption that C_{DIS} is proportional to the vapour pressure through the Henry constant[20,60]. Here, the purge gas should not disturb the equilibrium of the truly dissolved with the C_{COC} and/or C_{POC} limiting the application. This method does not apply for high K_{OW} values as they generally go together with low vapour pressures[61].

For the fluorescence quenching method the COC does not have to be separated from the C_{DIS}. The method is mainly applied for polyaromatic hydrocarbons and based on the quenching of the fluorescence signal because of binding to COC[62]. Incomplete quenching of the bound fraction can easily surpass a small truly dissolved content.

In general, all methods described above become inaccurate for very high K_{OW} values ($>10^6$) when the truly dissolved fraction is negligible compared to the bound fraction (Figure 2). In addition, the C_{DIS} will be often below the limit of detection, especially in unspiked studies. Addition of contaminants, which is done in almost all studies, only improves detectability but does not positively affect separation of phases.

An alternative method which is limited to the determination of K_{POC} involves the addition of a cosolvent like acetone, methanol, etc. Measuring the "K_{POC}" at different cosolvent fractions, the K_{POC}, for water only, can be found by log–linear extrapolation.[63]. The solubility of hydrophobic compounds increases exponentially with the cosolvent fraction[35]. The K_{POC}, therefore, decreases exponentially with increasing cosolvent fraction[64,65]. The advantages are lower adsorption to bottles, filters, etc.[1] Hence,[2] even more profitable is the decrease in COC adsorption, while the truly dissolved concentration increases and rapidly outnumbers the COC bound. It is not clear how a cosolvent affects the nature of POC.

The variability for higher K_{POC} values is generally due to the pitfalls in the methodology. However K_{POC} values also show a limited dependency on the nature of the organic matter[66]. Studying the literature on COC binding it appears to the author that the large variation in reported K_{COC} values are caused by both differences in sorption properties due to natural variations[55,67] as well as invalid definition of the COC content[17]. Research on COC fractionated by ultrafiltration might be fruitful as it can identify the COC responsible for adsorption[68]. Developing practical methods for characterization and estimation of COC is necessary for a better quantification of the distribution of contaminants in the waterphase[44,55,69].

Legislation

Two main sampling problems are of concern with respect to legislation. The first is ensuring representative sampling in both time and place and the second is performing accurate handling, storage and analysis of the sample. Strategies to accomplish representative sampling are not within the scope of this paper. In practice the feasible number of samples is often determined by the costs of sampling and analyses. Considering the filtering problems, the legislator can hardly prescribe filtration. For
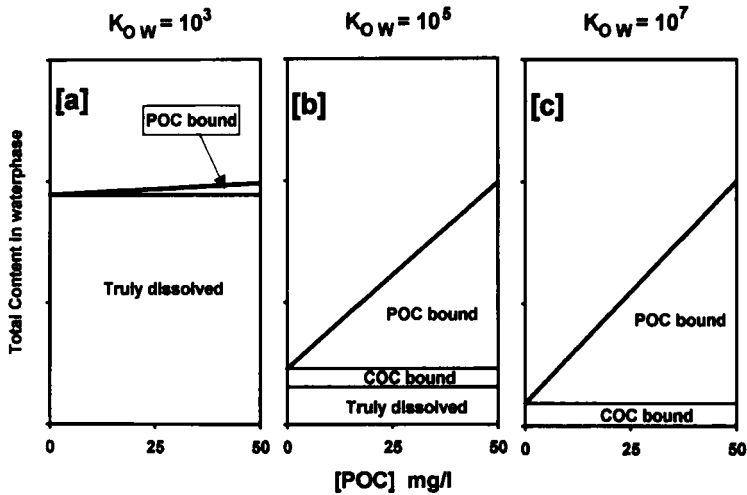
Figure 4 The relation between the C_{TOT} and [POC] for the K_{ow} values 10^3 [a], 10^5 [b] and 10^7 [c]. The [COC] is fixed at 5 mg/L.

waste water and drinking water intake there is no scientific need to do so. Limitations on extraction methods as described above should be taken into account. Application of cosolvents can favour analytical reliability.

Contamination level and environmental quality

For surface waters which are obliged to meet certain limits the legislator must be aware that meteorological and hydrodynamical conditions cause a high variability of the POC content, which is reflected in a variable C_{TOT}. To compare results from different situations with regard to the contamination level this variability has to be corrected for. In Figure 4 the relation between the [POC] and the C_{TOT} (thick line, arbitrary units) is given for K_{ow} 10^3, 10^5 and 10^7 (resp. Figure 4a, b and c) defining $K_{ow} = K_{POC} = K_{COC}$ and assuming that the COC content is fairly constant for a given situation as the influence on it by hydrodynamics is limited. In Figure 4a, $K_{ow} = 10^3$, there is no significant increase of C_{TOT} with increasing [POC] while C_{TOT} is nearly equal to C_{DIS}. On the other hand, for $K_{ow} = 10^7$ a strong slope is found with an intercept representing mainly the COC bound content (Figure 4c). The C_{DIS} is minimal and therefore invisible. In the Figure 4b K_{ow} $=10^5$ shows an intermediate case with a lower slope and an intercept of mainly truly dissolved and a minor COC bound content. These relations can be the basis for correction. With a number of results from whole water samples with different POC contents, regression analysis will provide a slope and an intercept. The slope represents the C_{POC} and the intercept is the sum of the truly dissolved and the COC bound. This is clear when writing the mass balance for C_{TOT}.

$$C_{TOT} = [POC] \, C_{POC} + [COC] \, C_{COC} + C_{DIS} =$$

$$[POC] \, K_{POC}C_{DIS} + [COC] \, K_{COC}C_{DIS} + C_{DIS} \qquad (11)$$

Under equilibrium conditions the C_{POC} is perfectly representing the contamination level. Principally, all three parameters are suitable for measuring the contamination level as they are related through partitioning. Hence, the determination of C_{COC} cannot be reliable as outlined above. In practice, the C_{DIS} and C_{POC} values are supplementary as for a given C_{TOT}, when C_{POC} is small, C_{DIS} is large, and viceversa. Determining the C_{POC} through the slope of C_{TOT} with POC, for low or intermediate K_{OW} values (Figure 4a), is inaccurate, as generally the precision of environmental analysis of total samples in not sufficient. However, collecting SPM by means of a continuous–flow centrifuge or filtration, the C_{POC} can be accurately determined for compounds with K_{OW} values as low as 10^3, since the C_{POC} is still 1000 times higher than C_{DIS}. Therefore, it is suggested that the contamination level for contaminants with $K_{OW} < 10^4$ should be determined by the dissolved phase, provided that the POC+COC content is <10 mg/L (Figure 1), and for $K_{OW} > 10^3$ by the suspended matter content (C_{POC}). In the overlap area from 10^3 to 10^4 both can be used.

As C_{POC} is much higher compared to C_{DIS}, analysis is more reliable and analytical methods and quality control procedures developed for sediments can be applied. The C_{POC} controls the truly dissolved through the K_{POC} and can be used to investigate spatial and temporal differences. Continuous–flow centrifugation is the most appropriate method for collecting SPM as it does not suffer from adsorption and an almost unlimited amount of water can be processed. Further, the organic carbon fraction can be determined in the same sample as well as the contaminants, grain size distribution, etc...

Fluxes of contaminants

Two main types of fluxes can be distinguished, i.e. water flowing continuously in one direction, like upstream in a river, and an alternating direction of the flow as appears in an estuary because of the tide. Methods for flux calculation, sampling strategies, number of samples in time and place, are beyond the scope of this paper. In addition, only consideration for sampling in the one direction case are discussed. Nevertheless, the conclusions hold for estuaries also.

In general, the whole waterphase can be sampled for contaminants with a $K_{OW} < 10^4$ as they will be mainly dissolved except for extreme POC contents (Figure 1). For $\log K_{OW} > 10^4$ the settling and dissolved (nonsettling) fractions have to be regarded separately. Application of continuous–flow centrifugation is prefered over filtration to separate between the settling and non settling flux. The time integrated character of the sampling can be of advantage. Additionally to the problems of adsorption and clogging, filtration will add the larger low density particles to the SPM content, however, they are transported like dissolved. To determine fluxes the contents in the centrifugates (truly dissolved and COC bound fraction) is actually transported like water and can be analyzed as such.

From eq 10 an estimation of the distribution can be made in advance (Figure 3). To determine the flux of POC bound contaminants, the POC-flux should be accurately determined. Because of fluctuating meteorological and hydrodynamical conditions the [POC] is more variable than the C_{POC} which is related to C_{DIS} (eq 2). Therefore, many determinations of [POC] are necessary to estimate an accurate carbon flux, while the C_{POC} of contaminants has to be determined only a limited number of times to achieve the same accuracy. For the determination of the POC flux the application of filtration is nearly inevitable due to the large number of samples. However, application of time integrated and/or riverflow related sampling with a continuous–flow centrifuge could be

a better alternative. After making the best estimate of the particulate organic carbon flux the particulate contaminant flux can be calculated through a few C_{POC} measurements. Of course, if the dissolved phase contributes, i.e. more than 10%, it has to be added to obtain the total flux.

In estuaries, nearly the same considerations apply except that the particulate carbon flux results from the difference between the incoming flux from sea and the outgoing flux. As these differences are sometimes in the order of only 10%[11], the dissolved phase, which normally can be neglected when it is less than 10% compared to the particulate phase (eq 10), can change from a minor into a major flux.

In these cases, whereas estimating fluxes seems a masterpiece it could be wondered whether it would not be better to look at the quality of the exported water instead of the amount of contaminant passing. The flux in these cases is generally determined by nature and will not be influenced by measuring it. Therefore, it might be a sound assumption that if the contamination level decreases the flux will decrease also.

CONCLUSIONS

The sampling of the waterphase with regard to the contamination level or environmental quality should be focused on the truly dissolved phase either by direct measurement or by measuring the C_{POC} as this value determines the truly dissolved content through the K_{POC}. Collection and analysis of suspended matter is preferred for organic compounds with a K_{OW} values $> 10^3$ and, subsequently, expressing the contaminant content per weight units organic carbon. For K_{OW} values $< 10^4$ the dissolved phase can be sampled. In that way all pitfalls described are avoided and results achieved in this way allow temporal an spatial comparisons. This approach should be recognized by the legislator and regulations should be made for suspended matter. There is a lack on accurate K_{POC} values for contaminants with K_{OW} values $> 10^7$ mainly due to limitations in methodolgy. When agreement can be achieved on the determination of COC and K_{COC} values, the dissolved phase can be normalized for the COC content.

In the measurement of fluxes of mainly adsorbed contaminants the effort should be concentrated on determining the POC flux. Moreover, the COC can contribute considerably to the flux. The quality approach on fluxes should be considered.

The application of continuous–flow centrifugation for both environmental quality as well as flux estimations is highly recommended.

Glossary

C_{DIS} Truly dissolved content (kg/L)
C_{COC} Contaminant content in COC expressed on organic carbon (kg/kg)
C_{POC} Contaminant content in SPM expressed on organic carbon (kg/kg)
C_{TOT} Contaminant content in total water sample (kg/L)
[COC]   Content of organic colloidal material in the waterphase (kg/L)

F_{COC} COC bound fraction in the waterphase
F_{DIS} Dissolved fraction in the waterphase
F_{POC} Particulate organic carbon bound fraction
f_{OC} Fraction of organic carbon in SPM
K_{COC} Partition coefficient for COC adsorption (L/kg)
K_{APP} Experimentally defined partition coefficient between dissolved and particulate (L/kg)
K_{OW} Octanol–water partition coefficient
K_{POC} Partition coefficient for POC adsorption (L/kg)
K_P Partition coefficient for SPM adsorption (L/kg)
[POC] Particulate organic carbon content in the waterphase (kg/L)
[SPM] Suspended particulate matter content in the waterphase (kg/L)

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