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Air/Water Exchange Dynamics of 13 Volatile Chlorinated C1- and C2-Hydrocarbons and Monocyclic Aromatic Hydrocarbons in the Southern North Sea and the Scheldt Estuary

JO P. DEWULF AND
HERMAN R. VAN LANGENHOVE*

Department of Organic Chemistry, Faculty Agricultural & Applied Biological Sciences, University of Ghent, Coupure Links 653, B-9000 Gent, Belgium

LUDO F. VAN DER AUWERA

Royal Meteorological Institute, Ringlaan 3, B-1180 Brussels, Belgium

Whereas a lot of marine research work has been done on heavy metals and semivolatile organic compounds, far less attention has been paid to the fate of volatile organic compounds in this area. This work focuses on 13 volatile organic compounds in marine waters and the marine atmosphere. During six campaigns in September 1994–December 1995, simultaneous air and water sampling was carried out in both the southern North Sea area and the Scheldt Estuary. Mean water concentrations for individual compounds were in the 2.2–72.9 ppt range ($n = 38$), whereas atmospheric concentrations varied between 2.3 and 854 pptv. Samples from the Scheldt Estuary proved to have elevated concentrations of chlorinated compounds. A number of water and air samples showed enhanced concentrations of C₂-substituted monocyclic aromatic hydrocarbons, which could not clearly be linked to anthropogenic activities. Back-trajectory calculations showed that a number of over sea atmospheric samples were affected by atmospheric transport from industrial sites, 250–300 km up wind. Fugacity modeling showed that the North Sea acts as a source to the atmosphere, not as a sink. Mean water to air mass transfer rates varied between 0.6–52.7 $\mu\text{g m}^{-2} \text{ day}^{-1}$ for all VOCs. It was statistically shown that water to air exchange rates of tetrachloroethylene, benzene, and toluene were slowed when air masses from continental origin were at the marine sampling sites instead of air masses from remote non-continental origin.

Introduction

The North Sea (746 000 km², Figure 1) is a marine system subjected to a number of anthropogenic activities. It receives 3.25×10^{11} ton year⁻¹ water via riverine input from a catchment area of 1.64×10^8 inhabitants (1). Next to riverine contributions, potential input of anthropogenic pollutants

are atmospheric/water transfer, offshore oil and gas production, and shipping. The North Sea Quality Status Report (1) summarizes input and concentration data on anthropogenic compounds such as heavy metals, PCBs, tributyl tin, PAHs, and pesticides in the North Sea. Information on the burdens of these compounds in marine systems is extensive. Additionally, for some groups of pollutants, air/water exchange studies are carried out, providing a better understanding of the dynamics of the pollutants. Such studies have been made for the Great Lakes in Canada for PCBs (2–6), PAHs (5, 6), and hexachlorocyclohexanes (7). An overview on air/water exchange dynamics of PCBs, HCHs, DDTs, chlordanes, and toxaphene is given by Bidleman and McConnell (8).

However, as it was stated in the Ministerial Declarations of the International Conferences on the Protection of the North Sea (9, 10), a number of volatile organic compounds are also of concern. In the 36 high-priority compounds list, six chlorinated C1- and C2-hydrocarbons (CHCs) are mentioned [chloroform (CHCl₃), tetrachloromethane (CCl₄), 1,2-dichloroethane (DCE12), 1,1,1-trichloroethane (TRI), and tri-(TCE) and tetrachloroethylene (TTCE)] next to heavy metals, pesticides, organotin compounds, pentachlorophenol, and dioxins. Additional priority lists of the Conferences formulated the need to investigate other CHCs, like 1,1-dichloroethane (DCE11), and a number of monocyclic aromatic hydrocarbons (MAHs), such as benzene (BENZ), toluene (TOL), ethylbenzene (ETBEN), *o*-xylene (OXYL), and *m*- and *p*-xylene (MPXYL).

Up to now, human activities are considered to be the main sources of the mentioned CHCs and MAHs, although a limited number of publications indicate natural sources for some of these compounds (11–15). However, despite the need to acquire more information on CHCs and MAHs (9, 10, 16) and despite their known impact on several atmospheric (17, 18) and biological systems (19–21), information on the concentrations of CHCs and MAHs in the marine environment and especially on the dynamics of these pollutants is limited. Available data on atmospheric and water column concentrations of a number of CHCs and MAHs were recently reviewed (22, 23).

This work focuses on atmospheric and water column concentrations of seven CHCs and six MAHs in the southern North Sea area (Belgian Continental Shelf), up to 60 km offshore, and in the Scheldt Estuary (Figure 1). The river Scheldt is one of the main riverine contributions to the southern North Sea with a catchment area of 21 000 km² and a population of 1×10^7 people in The Netherlands, Belgium, and France. The estuary provides marine access to Antwerp, which is one of the main harbors in Western Europe. During 1.5 yr, air and water samples were taken simultaneously in the southern North Sea and the Scheldt Estuary. The obtained results were interpreted by involving air/water equilibrium partitioning data and the development of a fugacity model. The role of the sediment compartment is assumed to be limited due to the low sorption degree of the VOCs (24). So the current approach, focusing on air/water exchange dynamics of these pollutants, gives a relevant view on the main physical chemical processes of VOCs in the marine environment.

Materials and Methods

Sampling and Analysis. *Sampling.* Samples were taken on board the Belgian RV Belgica. A map of the sampling sites in the southern North Sea (Belgian Continental Shelf) and in the Scheldt Estuary is presented in Figure 1. During six campaigns (September 1994, December 1994, March–April

* Corresponding author telephone: 32 9 264 59 53; fax: 32 9 264 62 43; e-mail: herman.vanlangenhove@rug.ac.be.

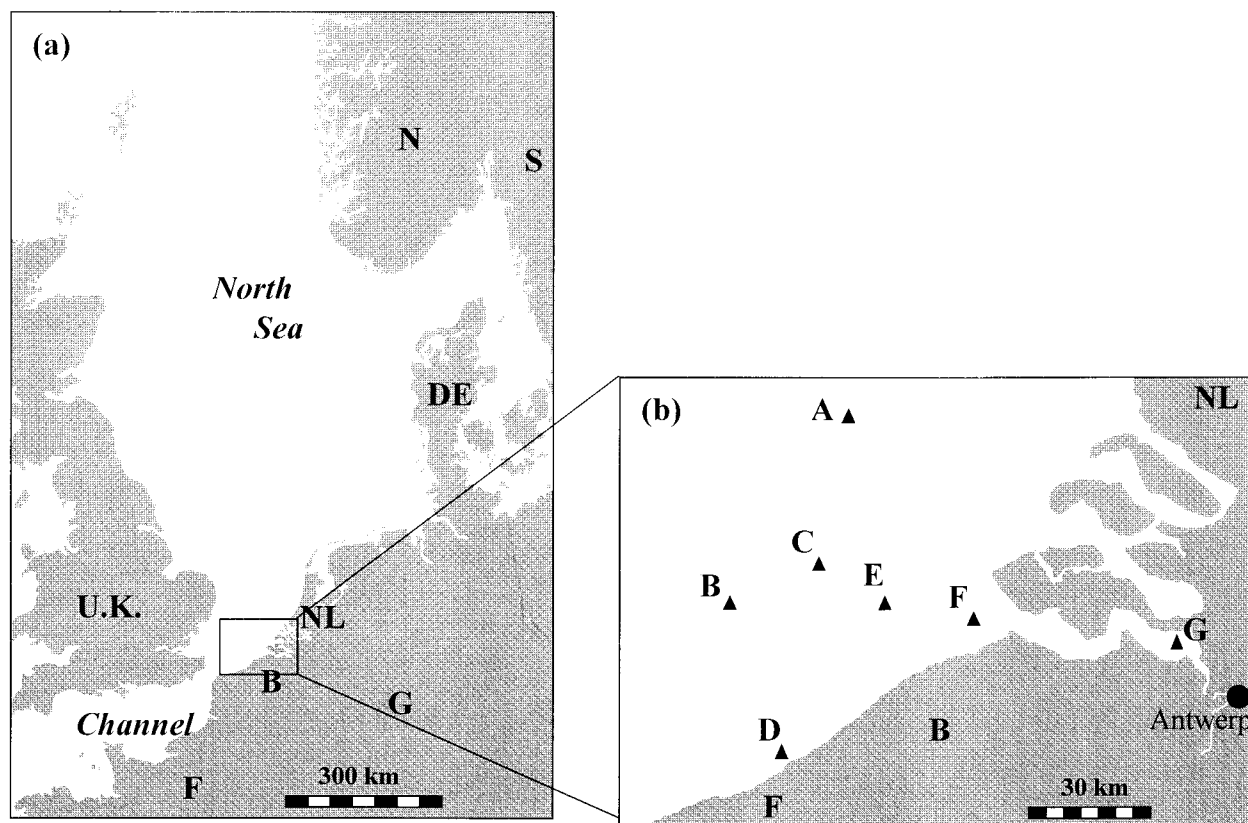


FIGURE 1. (a) Map of the North Sea area. (b) Sampling locations in the southern North Sea and Scheldt estuary, with locations indicated: A (51°50.83' N; 2°52.00' E), B (51°28.83' N; 2°27.00' E), C (51°34.84' N; 2°47.42' E), D (51°11.10' N; 2°42.07' E), E (51°28.27' N; 3°03.48' E), F (51°25.90' N; 3°17.80' E) and G (51°21.90' N; 4°13.50' E).

1995, May 1995, October 1995, and December 1995), all locations indicated in Figure 1 were sampled. Due to bad weather conditions, locations A, B, C, and E were not sampled in December 1994 so that in total 38 simultaneous air and water samples were taken. Air was sampled on the top of the wheel house of the vessel with the vessel positioned against the wind in order to avoid interferences from the vessel itself. Duplicate samples were taken at a rate of 200 mL min⁻¹ during 25 min on multisorbent tubes, consisting of open glass tubes (length 16 cm, o.d. 1/4 in.), filled with 170 mg of Carboxpack (graphitized carbon black, 100 m² g⁻¹, 60/80 mesh, Supelco) and 350 mg of Carboxieve III (carbon molecular sieve, 820 m² g⁻¹, 60/80 mesh, Supelco), and sealed with 1/4-in. brass end caps and Teflon ferrules (Alltech Assoc.). Before sampling, an internal standard (toluene-*d*₈) was brought onto the sorbent tubes after conditioning at 270 °C with helium (50 mL min⁻¹) for 4 h. Simultaneously, Teflon ferrules were conditioned in glass tubes (i.d. = 1 cm). This was necessary because it was proven that unconditioned Teflon ferrules contaminated the sorption tubes (25).

Water samples were taken by means of Niskin sampling bottles (5 or 10 L, General Oceanics Inc., Florida), generally at depths between 3 and 5 m. Samples were transferred to 0.75-L dark bottles, which were completely filled to avoid headspace. Microbial degradation was prevented by the addition of HCl (6.25 N) to obtain pH ≤ 2. Chloroform-*d* and toluene-*d*₈ were added as surrogates (at 96.2 and 60.5 ppt, respectively). Subsequently, samples were stored at 4 °C onboard until shipment to the laboratory (26).

Water Sample Analysis. VOCs were purged out of a 60-mL sample onto a Vocab 4000 sorbent trap (Supelco) in an off-line construction, in which a water trap, consisting of a stainless steel tube kept at -11 ± 1 °C, was inserted between the purge vessel and the sorbent trap. Thermal desorption was carried out in an on-line CDS Peakmaster system (CDS

Analytical Instruments, Oxford). After cryofocusing, separation and detection were carried out in a Carlo Erba QMD1000 system (Carlo Erba Instruments, Milan, Italy), where the VOCs were separated on a RTX-502.2 capillary column [poly-(dimethyl(80%)/diphenyl(20%) siloxane)] (Restek) and detected in the selected ion monitoring mode. The 13 compounds detected were CHCl₃, CCl₄, DCE11, DCE12, TRI, TCE, TTCE, BENZ, TOL, ETBEN, OXYL, and MPXYL. Limits of detection for the target compounds varied between 0.5 and 1.25 ng L⁻¹, except for CHCl₃ (4.9 ng L⁻¹), BENZ (4.8 ng L⁻¹), and TOL (2.7 ng L⁻¹) due to nonblank signals for these latter compounds. For these three target compounds, corrections for the nonblank signal were made. Reproducibility tests on standards showed relative standard deviations below 11% for all VOCs except for DCE12 (15.7%) (*n* = 10). Quality assurance was enhanced by the application of quality control charts and standard addition tests, as proposed by QUASIMEME (27). Recoveries of the surrogates CDCl₃ and C₇D₈, added on board the vessel during sampling, were 106.1 ± 26.8 and 107.2 ± 24.5%, respectively (*n* = 38). So the whole technique, including sample storage and treatment and the analytical approach, proved to be accurate at the ppt level and avoided losses during the whole procedure. More detailed information can be found in a previous paper (26).

Air Sample Analysis. Air sampling tubes were desorbed in an off-line thermal desorption system onto a Vocab 4000 trap. A wet trap was inserted in front of the Vocab 4000 trap. The sorbent trap was analyzed with the same thermal desorption-gas chromatograph-mass spectrometer system as used for the water analyses. Calibration of the samples was done by means of the closed two-phase system (25). In this method, headspace of an equilibrated air/water system is transferred to a sorbent sampling tube, which was subsequently analyzed. Limits of detections were in the 2.2–5.7 ng m⁻³ range, except for CHCl₃ (41 ng m⁻³), BENZ (96 ng

m⁻³), and TOL (49 ng m⁻³). Reproducibility tests on standards (2.2–4.1 µg m⁻³) showed relative standard deviations below 8% ($n = 4$). Details can be found in previous work (25).

Development of the Fugacity Model. *Fugacity and Fugacity Capacities.* Physical chemical behavior of the target compounds was studied by application of the fugacity model (28–31). Sorption of the target compounds on the sediment layer was assumed to be negligible in view of the low log K_{ow} values (32). This was experimentally confirmed as described in a previous paper (24). So the modeling focused on the air and water compartments. The fugacity f_i (Pa) in the compartment i is defined as

$$f_i = \frac{C_i}{Z_i} \quad (1)$$

where C_i is the concentration in compartment i (mole m⁻³) and Z_i is the fugacity capacity of the compartment for compound i (mol m⁻³ Pa⁻¹). The fugacity capacities of the air (Z_a) and water (Z_w) compartments are

$$Z_a = \frac{1}{RT_a} \quad Z_w = \frac{1}{HRT_w} \quad (2)$$

where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T_a and T_w are the respective temperatures (K), and H is the Henry's law constant (dimensionless).

The Henry's law constant H depends on the salinity (S , in g L⁻¹) and the temperature (T , in K) of an air/water system (33):

$$H = \exp(aT^{-1} + bS + c) \quad (3)$$

where a , b , and c are regression constants. Salinity data were obtained from the database of the Management Unit of the North Sea Mathematical Models (34). In real systems, water and air can be at different temperatures, so that the Henry's law constants, determined in laboratories at equal temperatures for both phases, cannot be imported promptly. From theoretical considerations, it is found that the chemical potential μ (J mol⁻¹) of a gas is dependent on its pressure P (atm) (32):

$$\mu = \mu^0 + RT \ln \left(\frac{P}{P^0} \right) \quad (4)$$

where μ^0 and P^0 are the chemical potential (J mol⁻¹) and vapor pressure (atm) in the reference state, respectively. So the chemical potential of a gas at two different temperatures T_a and T_w is equal if

$$T_a \ln P_a = T_w \ln P_w \quad (5)$$

or

$$P_a = P_w^{T_w/T_a} \quad (6)$$

From the monthly averaged data for the studied area (35), it was found that T_w/T_a varied between 0.98 and 1.02. So if one notes that $T_w/T_a \approx 1$, then the latter equation can be approximated as $P_a = P_w$. So from the gas law and the previous considerations, the gas-phase concentration $C_{a, \text{at } T=T_w}$ can be noted as

$$C_{a, \text{at } T=T_w} = C_{a, \text{at } T=T_a} \frac{T_a}{T_w} \quad (7)$$

So the in situ air/water equilibrium distribution ratio H' is

$$H' = \frac{C_{a, \text{at } T=T_a}}{C_{w, \text{at } T=T_w}} = \frac{C_{a, \text{at } T=T_a}}{C_{w, \text{at } T=T_w}} \frac{C_{a, \text{at } T=T_w}}{C_{a, \text{at } T=T_w}} \quad (8)$$

or

$$H' = \frac{T_w}{T_a} H_{T=T_w} \quad (9)$$

H' values were calculated in this way. It can be seen that H' can also be approximated by $H_{T=T_w}$ since $T_w/T_a \approx 1$.

Diffusive Water/Air Exchange Process. From the development of the fugacity model (30), the empirical relation between the mass transfer of VOCs and of oxygen (32, 36), and the relationship between the wind speed and the mass transfer of oxygen (32), the diffusive water to air exchange rate N (mol s⁻¹) is calculated from

$$N = \frac{A}{HRT_w} \left(\frac{D_{w, \text{voc}}}{D_{w, \text{o}_2}} \right)^{0.57} (4 \times 10^{-6} + 4 \times 10^{-7} u_{10}^2) (f_w - f_a) \quad (10)$$

where A is the interphase area (m²), u_{10} is the wind speed (in m s⁻¹, at height = 10m), and $D_{w, \text{voc}}$ and D_{w, o_2} are the diffusion coefficients of the VOC and oxygen at temperature T_w . These diffusion coefficients can be calculated from the Othmer-Thakar equation (32).

Nondiffusive Water/Air Exchange Processes. Due to the high vapor pressure of the VOCs considered (>800 Pa at 25 °C), sorption on aerosols and by consequence dry deposition can be neglected (37). Since partitioning of VOCs between the atmosphere and raindrops reaches equilibrium after a fall of 10 m (38), wet deposition rates N_r (mol s⁻¹) can be calculated from the precipitation rate R (m³ m⁻² s⁻¹) (35) and the compounds air/water equilibrium partitioning constant $H_{T=T_a}$:

$$N_r = RC_a H_{T=T_a} A \quad (11)$$

Results and Discussion

Water Analyses. *Concentration as a Function of Depth.* In May 1995, a concentration profile of the target compounds was established for sampling location B for CCl₄, TCE, TOL, and ETBEN. Relative standard deviations are 10.3, 25.0, 9.3, and 15.2%, respectively ($n = 6$). No clear increasing or decreasing concentration gradient with depth was observed for any VOC. This can be explained by the shallowness of the southern North Sea (average depth 30 m) and the mixing of the water body by slow currents and wind effects.

Results of the Sampling Campaigns. Mean, 25, 50, and 75 percentiles of the concentrations of the data set of concentrations of the VOCs in all sampling campaigns are presented in Table 1. CCl₄, DCE11, TRI, and TTCE show 75P levels (75 percentile) below 7 ppt. These values are in the same range as background concentration levels found in the literature. At open sea locations and in coastal systems not affected by anthropogenic activities, concentrations are reported to vary between <1 and 5.8 ppt for CCl₄, between <1 and 11 ppt for TRI, and between <1 and 6 ppt for TTCE (23). Literature data of DCE11 are too scarce to be compared. The other CHCs (CHCl₃, DCE12, and TCE) show 75 percentiles between 15.5 and 45.3 ppt in the present data set. The higher 75 percentile levels may be partially explained by elevated concentrations of these compounds at location G in the Scheldt estuary. However, omitting values from G still results in a data set with 75 percentiles of 25.8 ppt for CHCl₃, 8.9 ppt for DCE12, and 15.0 ppt for TCE. These levels of CHCl₃ and TCE are higher than literature data (23). Additionally, from literature data on anthropogenic emissions of TRI, TCE, and TTCE, which are all in the same range (39, 40), it is unexpected

TABLE 1. Mean, 25, 50, and 75 Percentile Levels of the Data Set ($n = 38$) of the Concentrations of All VOCs in the Water Column (in ng L^{-1}) and in the Atmosphere (in pptv)

VOC	water				atmosphere			
	mean	25P	50P	75P	mean	25P	50P	75P
CHCl_3	72.86	10.19	17.55	45.35	19.0	9.4	13.9	19.7
CCl_4^a	2.22	1.33	1.69	2.23	98.4	70.2	91.0	129.2
DC11^b	2.28	1.14	1.14	2.88	2.3	1.4	1.9	2.7
DCE12	21.01	4.92	6.19	15.52	17.5	8.6	12.0	21.8
TRI	14.93	2.75	3.57	6.81	141.1	103.4	136.5	168.9
TCE	17.19	4.01	8.80	21.69	62.6	21.7	51.8	74.6
TTCE	19.96	1.69	2.68	4.54	45.0	26.5	39.7	64.3
BENZ	15.23	13.32	14.46	18.80	412.8	182.2	291.5	479.1
TOL	27.00	18.47	24.48	34.39	734.7	287.4	613.9	951.0
ETBEN	21.94	7.28	13.43	32.29	309.2	138.7	226.9	312.7
MPXYL	46.64	8.91	13.60	69.20	854.4	127.0	224.7	389.9
OXYL	23.19	7.78	12.39	40.34	526.0	87.9	157.6	277.9

^a Three data of the entire set of water column concentrations of CCl_4 are below the limit of detection ($=0.77$ ppt). ^b Twenty-five data of the entire set of water column concentrations of DCE11 are below the limit of detection ($=1.14$ ppt).

that TCE has higher concentrations than TTCE and TRI. In 1992, emissions of TRI, TCE, and TTCE are reported for Europe as 116 000, 96 000, and 104 000 ton, respectively (39, 40). Possibly the enhanced levels of CHCl_3 and TCE might be explained by natural emissions. Production of CHCl_3 and TCE by algae has been described in the overviews by Dewulf and Van Langenhove (23) and Gribble (41). In tropical oceans, the amount of biogenically produced CHCl_3 transferred to the atmosphere was estimated as 350 000 tons/year⁻¹ (42). More recently, production of CHCl_3 by macroalgae from shelf seawaters on the west coast of Scotland is reported (12). Similarly the production of TCE and minorly TTCE by various macroalgae and a microalga from temperate, subtropical, and tropical zones is mentioned (the production ratio of TCE/TTCE varies between 10 and 400) (13). The formation of CHCl_3 was explained by an intracellular chloroperoxidase system in which CHCl_3 is formed by the reaction of hypochlorous acid (HOCl) with organic matter (12).

MAHs interquartile ranges are higher than those of CHCs. Apart from some observations at locations directly affected by anthropogenic sources, literature data on levels of BENZ, TOL, ETBEN, MPXYL, and OXYL for coastal systems are in the 9.3–35, 4.5–100, <1–52, 2.5–66, and <1–42 ppt ranges, respectively (23). So the interquartile ranges of the data set presented here all vary within the literature data set, except the 75P of MPXYL (75P = 69 ppt). It is difficult to verify if concentrations in all coastal systems investigated, including the area investigated in this work, are enhanced due to anthropogenic activities when compared to remote background levels. Observations at remote sites are scarce (23). Only Sauer (43) measured BENZ and TOL in the Gulf of Mexico at a depth of 1000 m where concentrations of 1.6 and 1.5 ppt were found. In this respect, it must be emphasized that oil products are intensively transported overseas in coastal areas as is the case for the southern North Sea. Previous work on MAHs concentrations in coastal systems attributed the enhanced concentrations to marine traffic (44, 45).

Statistical Approach. A principal component analysis (PCA) with all VOCs as variables resulted in the extraction of three main factors. The factor loadings are presented in Figure 2a. It can be seen that factor 1 (which is mainly determined by DCE12, TRI, TCE, and TTCE) contributed 41.2% to the total variance. Factor 2, affected by C_2 -MAHs, and factor 3, associated mainly to CHCl_3 , DCE11, and CCl_4 , contributed 23.9% and 13.6%, respectively. So 78.6% of the

variance in the data set can be explained by three factors, containing all VOCs except BENZ and TOL.

Figure 2b shows the factor score plots of the samples. Whereas the major part of the samples shows scores below 0.0 on factor 1, all samples from location G in the Scheldt Estuary have scores between 1.1 and 2.9. The enhanced concentrations at G, at 25 km downstream of Antwerp, can be attributed to anthropogenic emissions of a number of CHCs applied in several industrial processes situated in and around Antwerp. Apart from the G samples, all samples show scores on factor 2 below 0.6, except five samples from the fourth campaign and one sample of the fifth campaign having scores ≥ 1 . The five samples of the fourth campaign have MPXYL concentrations over 100 ppt and ETBEN and OXYL concentrations over 40 ppt, being all equal to or over the 75 percentile of the entire set. Sample B/C5 is mainly distinguished by high OXYL concentration (63 ppt), which is over the 90 percentile level ($=50$ ppt). The enhanced concentrations of C_2 -MAHs cannot be explained promptly. In a first approach, direct anthropogenic emissions from local marine traffic could be suggested, since five cases were observed in the same campaign. However, this is unlikely since the origin of C_2 -MAHs (oil products) should give rise to associated enhanced concentrations of BENZ and TOL. An explanation may be found in natural marine sources, although limited literature data supporting this hypothesis can be found. A few papers mention natural sources of MAHs (11, 14, 15). Biogenic MAH production was explained by several pathways, but mainly by biological modification of terpenoid structures. Since it is known that marine organisms such as sponges and algae produce a series of carotenoid structures (46), the presence of enhanced concentrations of C_2 -substituted MAHs might be related to natural production. Moreover, during the fourth sampling campaign, algal bloom was observed visually and was confirmed by analysis (47). This hypothesis however need to be confirmed by more experiments.

Finally, the third factor distinguished five samples with scores over 0.5 whereas other samples have scores below 0, excluding samples from location G. Very high concentrations of CHCl_3 (>1000 ppt) were observed in sample E/C1. The high CHCl_3 concentrations can be associated to potential natural sources, as discussed previously. The PCA shows that CCl_4 and DCE11 have associated enhanced concentrations, although this is observed to a smaller extent.

Next to PCA, a multiple *F*-test on all VOCs for the factor sampling location was carried out. No single sampling location could be distinguished for CHCl_3 and CCl_4 nor for all MAHs ($\alpha = 0.01$ and $\alpha = 0.05$). For DCE11, DCE12, TRI, TCE, and TTCE however, location G showed significant enhanced concentrations ($\alpha = 0.01$ and $\alpha = 0.05$), confirming the factor 1 obtained in the PCA. The results of the test imply that, for the nonestuarine sampling locations, the distance to the coast (4–60 km off-shore) is not a factor significantly contributing to the variation in the concentrations of CHCs and MAHs.

Air Samples. Mean, 25, 50, and 75 percentile levels of the data set on atmospheric VOC concentrations from all sampling campaigns are presented in Table 1. Background levels over open sea locations were reviewed by Dewulf and Van Langenhove (22). The range of mentioned literature on CHCl_3 , CCl_4 , TRI, TCE, and TTCE were reported as 9–45, 71–166, 37–214, 1–22, and 1–60 pptv, respectively. The interquartile ranges of the data of this work for CHCl_3 , CCl_4 , TRI, and TTCE all vary within the background levels. So it can be concluded that the area studied is not affected in a more severe way than remote sites with respect to these compounds. DCE11 and DCE12 levels can hardly be compared to background levels since literature data on these VOCs are too limited.

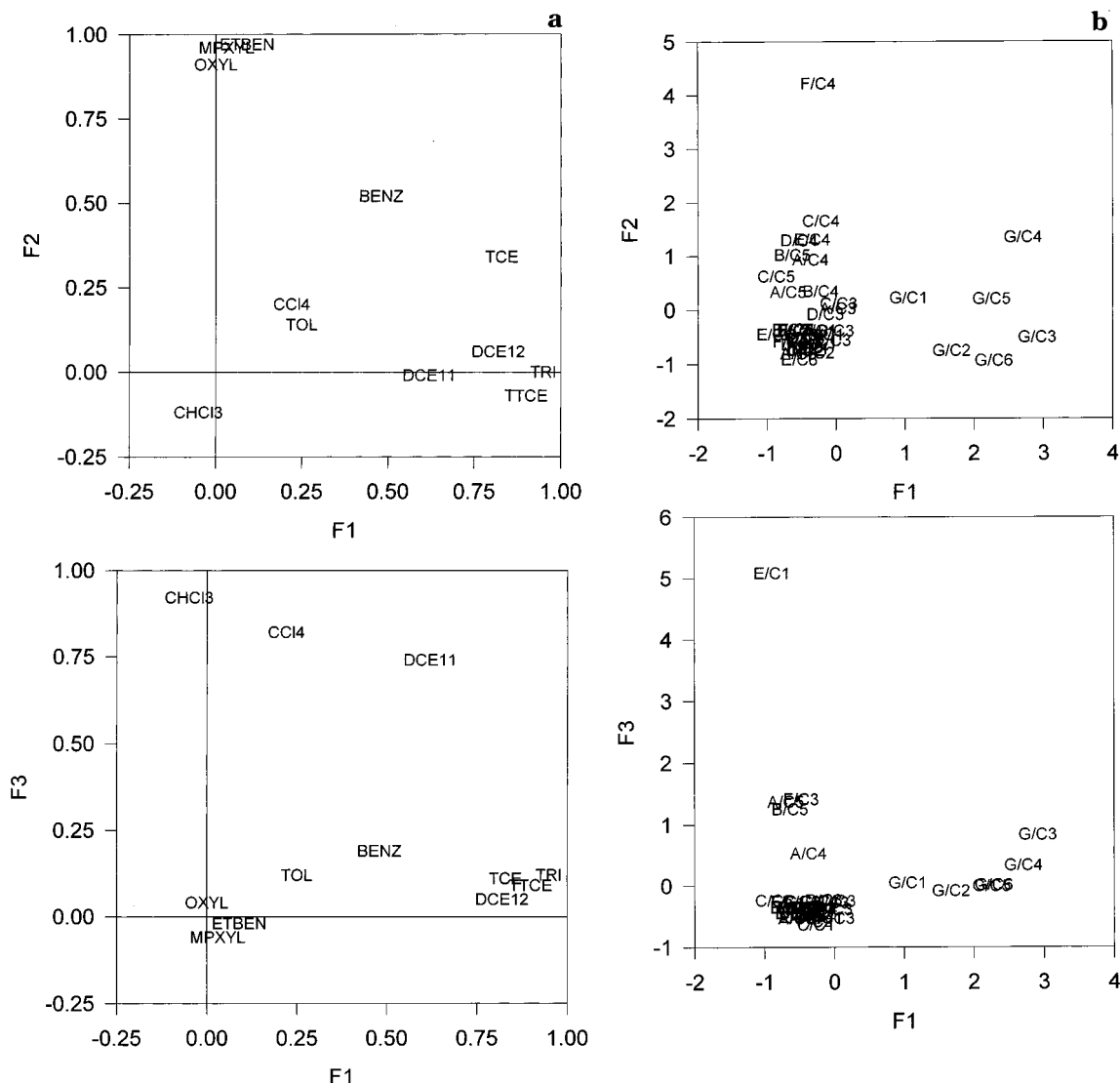


FIGURE 2. Principal component analysis on all water samples for all VOCs: (a) factor loading plots, contributions of each VOC to each factor (F1, F2, and F3); (b) factor score plots, scores of all samples on each factor (F1, F2, and F3). Samples are marked by Sampling location/Campaign number, where Sampling location is to be found in Figure 1, and Campaign number is as follows: C1 = September 1994, C2 = December 1994, C3 = March–April 1995, C4 = May 1995, C5 = October 1995, and C6 = December 1995.

According to the wind direction during sampling, data were split into two groups. The first group consists of samples for which the wind direction was from European continental origin (27 samples), whereas the second group consists of samples with northern North Sea or Atlantic origin, entering the area studied over sea or over the British Isles (11 samples). The interquartile concentration ranges of the VOCs for both groups are presented in Figure 3. The comparison of CHCs concentrations in air masses from continental and noncontinental origin shows slightly higher interquartile ranges for the group of samples from continental origin. A *t*-test indicates that TTCE concentrations in samples from continental origin are significantly higher than in sample matrixes from marine origin ($\alpha = 0.05$). Whereas concentrations of TCE at open sea locations are reported to be below 22 pptv (22), higher interquartile ranges are found in this work (22–75 pptv).

Concentration levels of MAHs are higher than those of CHCs, with interquartile ranges varying between 100 and 600 pptv (Table 1). From Figure 3 it can be seen that samples, taken in air masses from continental origin, give rise to enhanced concentrations when compared to samples from marine origin. A *t*-test showed that BENZ and TOL con-

centrations in the group of samples taken in air masses from continental origin are significantly higher ($\alpha = 0.05$). When the concentrations in the samples from marine origin are compared to concentrations determined in the free troposphere or at oceanic sites (22), they are of a higher level. This may be explained by a water to air transfer of MAHs brought into the marine environment by anthropogenic emissions from oil transport in this coastal area. The data presented here fit better to levels of concentrations observed at the coast of Brittany (France), where BENZ, TOL, ETBEN, MPXYL, and OXYL concentrations were in the 71–360, 160–650, 24–290, 37–410, and 18–180 ppt range, respectively (48).

PCA on all VOC concentration data was carried out. The factor loading plots are presented in Figure 4a, and factor score plots of the samples are given in Figure 4b. Factor 1 is mainly affected by C_2 -substituted MAHs and contributed 29.8% to the total variance; factor 2, mainly determined by TCE, TTCE and TOL, contributed 24.8% whereas factor 3, explaining 14.3% of the total variance, is mainly determined by $CHCl_3$, DCE12, and BENZ. According to factor 1, three samples of the fourth campaign are distinguished by high scores due to concentrations of C_2 -substituted MAHs in the 1–10 ppb range. The absence of associated enhanced

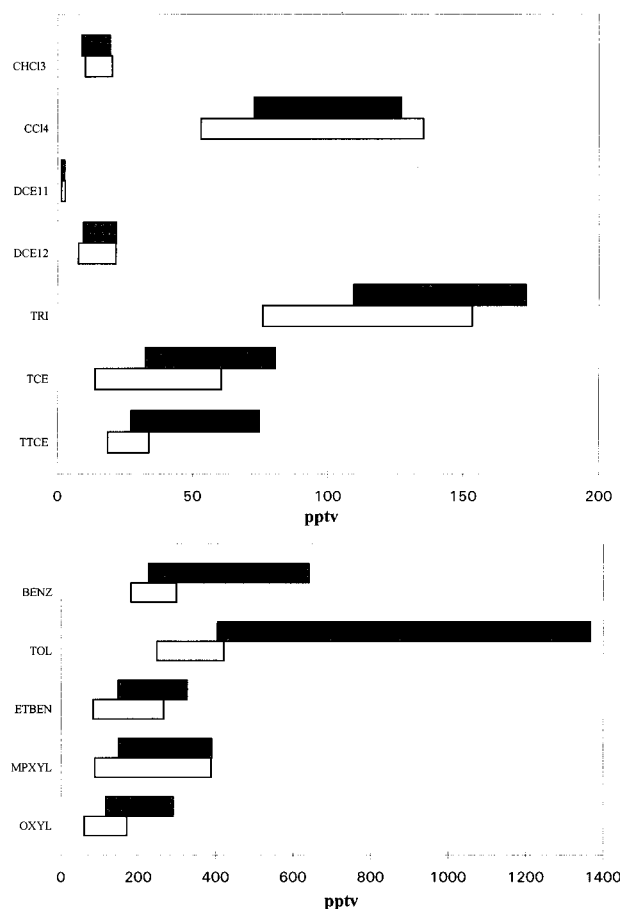


FIGURE 3. 25–75 percent ranges of atmospheric concentrations of all VOCs with blank boxes representing the data set of sampled air masses from non-European continental origin. Gray boxes are data from air masses from European continental origin.

concentrations of BENZ and TOL suggests that these high concentrations may not be due to anthropogenic sources. Moreover, sample B07/C4 is not from continental origin. Similarly to the water samples taken during the same campaign, it can be assumed that the enhanced concentration levels are caused by natural production in the aquatic compartment, followed by a water to air exchange.

Second, two samples are distinguished according to factor 2 by enhanced concentrations of TCE, TTCE, and TOL. Both samples are from air masses of continental origin, indicating the anthropogenic impact. This is also supported by enhanced concentrations (around and over the 75 percentile) of BENZ and ETBEN in the same samples. The wind direction and wind speed during sampling indicate that the air masses were coming over urban and industrial agglomerations in northern France. Also the samples A/C6, B/C6, and C/C6 are of continental origin, showing enhanced concentrations of CHCl₃, DCE12, and BENZ. Also here the anthropogenic source is reflected by the concentration level (around and above the 75 percentile) of other compounds (TTCE, TOL, and C₂-substituted MAHs). Data on wind direction obtained at the sampling sites indicate air masses probably coming from central western Europe, where German industrial activities are situated.

To confirm the potential links between origin and the five latter samples distinguished by PCA, back-trajectory calculations were carried out. The air masses sampled in D/C5 and B/C5 are affected by contributions of the Paris agglomeration and the cities and industrial sites of Nantes, Rennes, Caen, and Le Havre. Samples A/C6 and B/C6 proved to be taken in air masses coming over the highly industrialized Ruhr

TABLE 2. Mean, 25, 50, and 75 Percentile Levels for the Complete Data Set ($n = 38$) for Air to Water Fugacity Ratios (ratio = f_a/f_w , dimensionless) and Water to Air Exchange Rates (flux, $\mu\text{g m}^{-2} \text{d}^{-1}$)

VOC	ratio				flux			
	mean	25P	50P	75P	mean	25P	50P	75P
CHCl ₃	0.07	0.02	0.04	0.10	52.7	4.4	12.2	27.3
CCl ₄	0.58	0.31	0.47	0.81	0.6	0.2	0.5	0.7
DCE11	0.05	0.02	0.04	0.06	1.2	0.5	0.7	1.5
DCE12	0.42	0.08	0.25	0.53	7.2	1.2	2.5	8.3
TRI	0.46	0.17	0.40	0.70	5.4	0.4	1.2	2.8
TCE	0.41	0.03	0.10	0.45	8.0	1.1	6.6	9.4
TTCE	0.30	0.10	0.22	0.44	6.7	0.6	1.1	2.2
BENZ	0.80	0.28	0.45	0.84	3.9	1.1	4.7	7.7
TOL	0.71	0.29	0.56	1.05	4.4	−0.6	6.3	9.6
ETBEN	0.52	0.19	0.49	0.72	7.2	1.0	3.4	11.8
MPXYL	0.56	0.12	0.38	0.74	9.5	1.6	4.7	18.4
OXYL	0.90	0.16	0.43	0.95	0.8	0.2	3.6	8.3

area (Germany). Finally, sample C/C6 is affected by contributions of the western German Saar area and Brussels. So, in conclusion, it has been shown that air masses at marine sites can be significantly affected by continental human activities, being approximately at a distance of 250 km (Paris) to 300 km (Ruhr area).

Air/Water (dis)Equilibrium. The air/water equilibrium is expressed by Henry's law coefficient, which is dependent on the air and water temperature and the salinity, as discussed in the development of the fugacity model

$$H = \frac{T_w}{T_a} \exp(aT_w^{-1} + bS + c) \quad (12)$$

where the coefficients were studied in detail in previous work (33). From the obtained concentration data and the environmental parameters, the air to water fugacity ratios $R = f_a/f_w$ were calculated. So $R > 1$ indicates deposition, $R = 1$ reflects equilibrium, and $R < 1$ indicates volatilization from the water compartment. Mean data and 25, 50, and 75 percentile levels of the complete data set for R values are presented for all VOCs in Table 2.

All interquartile ranges of R are below 1.0 for all VOCs, except for TOL (75P = 1.05). So in general, a disequilibrium is found with oversaturation in the water phase. Aromatic compounds show mean fugacity ratios between 0.52 (ETBEN) and 0.90 (OXYL). Extreme low ratios (interquartile ranges of R below 0.1) are noticed for CHCl₃ and DCE11. The degree of disequilibrium for CHCl₃ confirms the previous discussion on the potential natural production of CHCl₃ in the water column. Interpretation of data on DCE11 is difficult since a number of data are based on concentrations that are detection limit values. The other CHCs show higher average fugacity ratios, i.e., between 0.30 (TTCE) and 0.58 (CCl₄). It is found that for DCE12, TRI, TCE, and TTCE all samples taken in the Scheldt Estuary show R ratios below 0.06, emphasizing the high air/water disequilibrium. Excluding these samples, the interquartile ranges of these compounds increase to 0.22–0.69, 0.26–0.79, 0.06–0.54, and 0.15–0.46, respectively (means: 0.50, 0.55, 0.49, and 0.36). Few literature data are available on air/water (dis)equilibrium distribution of VOCs in the marine environment. Water to air equilibrium concentration ratios of CCl₄ in the Atlantic were reported as $104 \pm 25\%$ (49).

Figure 5 represents the plot of f_w as a function of f_a for the compounds TTCE, BENZ, and TOL, which showed significant higher atmospheric concentrations in air masses from continental origin than in air masses from the other wind sectors. It is noticed that all values of R are below 1 for samples from noncontinental origin. Excluding the six

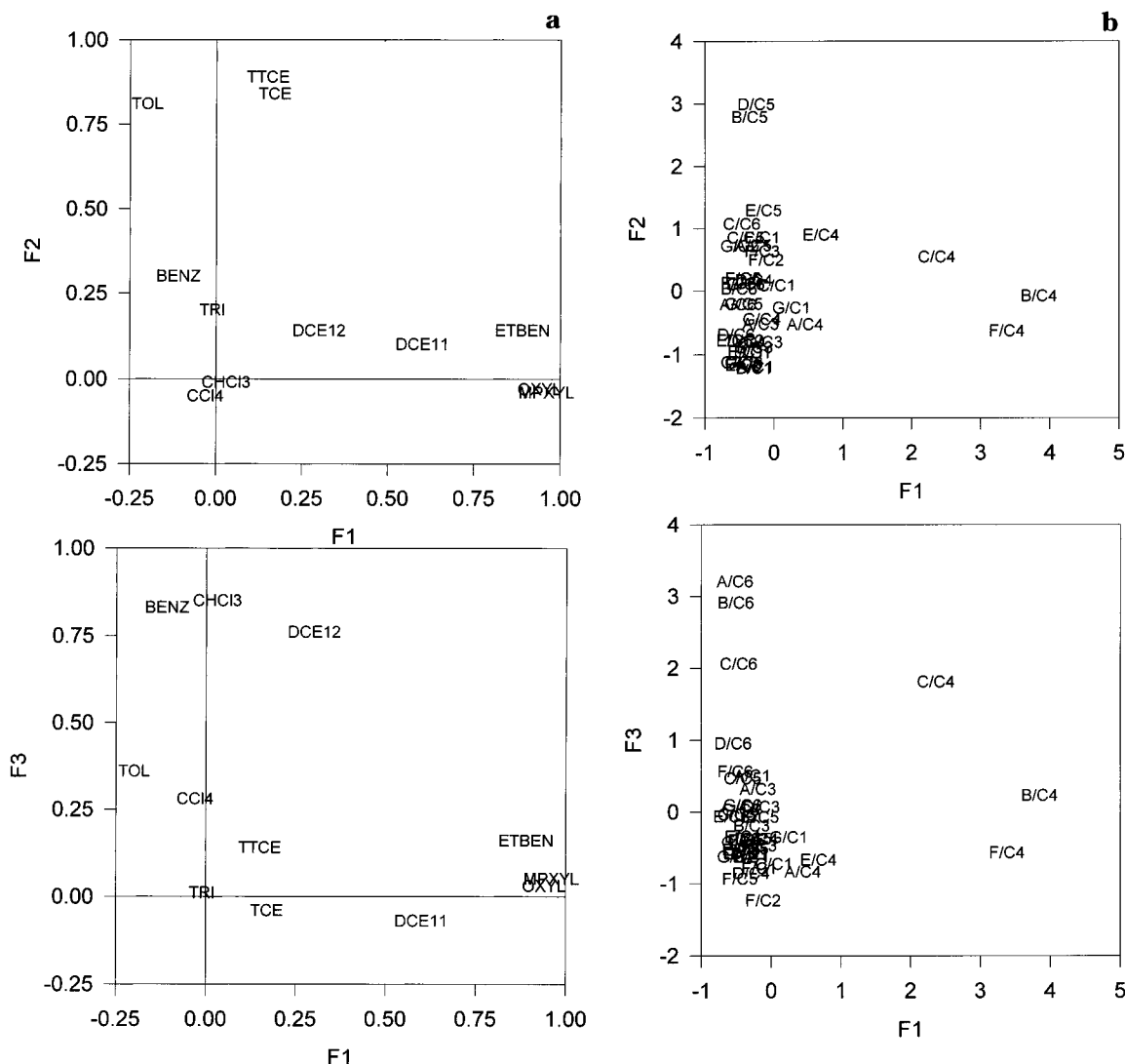


FIGURE 4. Principal component analysis on all air samples for all VOCs: (a) factor loading plots, contributions of each VOC to each factor (F1, F2, and F3); (b) factor score plots, scores of all samples on each factor (F1, F2, and F3). Samples are marked as in Figure 2.

samples of TTCE in the Scheldt Estuary, which are found as the points with the highest k_w , the mean R ratio over the three compounds for the samples with noncontinental air masses sampled is 0.28 (interquartile range 0.20–0.37) ($n = 29$), whereas the mean R value is 0.77 (interquartile range 0.29–1.04) for the subset of samples with air sampled from continental origin ($n = 79$). These two subsets are significantly different in a t -test at $\alpha = 0.01$. So this means that the water to air exchange is limited when the air masses above the North Sea are from continental origin due to enhanced atmospheric concentrations. On the other hand, the disequilibrium $R < 1$ is noticed for all cases with noncontinental air masses sampled. In conclusion, the North Sea usually acts as a source of VOCs to the atmosphere, which can be limited quantitatively when continental air masses are present.

Air/Water Exchange Velocity. From the application of the fugacity model, it was found that diffusive exchange was the main air/water mass transfer process. Calculations of the wet deposition rate proved to be below 1% of the diffusive exchange rate in all cases for all VOCs. The diffusive water to air fluxes are presented in Table 2. From the interquartile ranges, it is found that for all VOCs fluxes are in the -1 to $10 \mu\text{g m}^{-2} \text{d}^{-1}$ range (water to air), except for CHCl_3 , ETBEN, and MPXYL. The 75P levels are higher for these latter

compounds, which can be explained by potential natural contributions, as discussed previously.

The obtained exchange rates can hardly be compared to literature data on air/water exchange of VOCs. Bidleman and McConnell (8) reviewed data on air/water exchange of organic pollutants, including data on HCHs, DDTs, chlorodanes, and toxaphene. Most available data for these semi-volatile compounds vary between 0.5 and $150 \text{ ng m}^{-2} \text{d}^{-1}$, i.e., approximately a factor 10–10 000 lower than the results for VOCs presented in this work. The main factor explaining the difference in the magnitude of fluxes is to be found in the water concentrations, showing mean values between 2.22 (CCl_4) and 72.86 ng L^{-1} (CHCl_3), whereas concentrations of PCBs are reported between 0.1 and 6.7 ng m^{-3} (2–4). Second, the higher exchange rates of CHCs and MAHs are partially due to higher mass transfer coefficients. For VOCs, transfer velocity coefficients vary between 0.20 and 1.18 m d^{-1} in this work, whereas in the literature coefficients for PCBs are mentioned between 0.01 and 0.3 m d^{-1} (2–4). Finally, the degree of disequilibrium may be higher for VOCs than for compounds investigated in previous work. Jantunen and Bidleman (50), for example, reported water to air fugacity ratios of 1.86 and 0.74 for HCHs.

The obtained data set shows that the area investigated acts as a source to the atmosphere for the VOCs, with mean

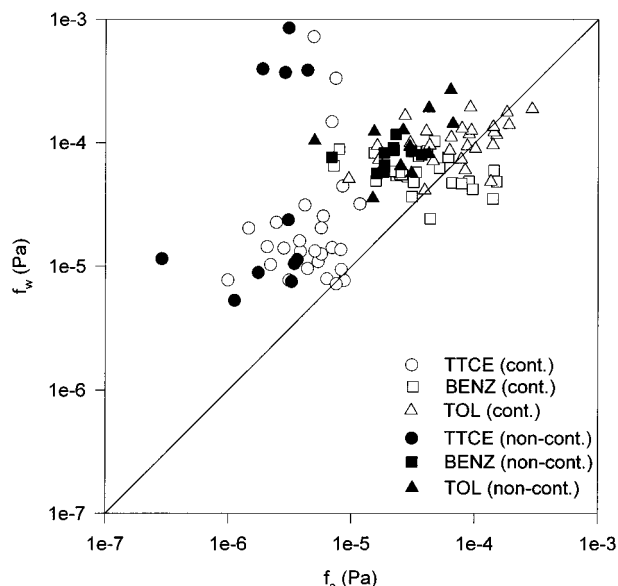


FIGURE 5. Plot of fugacity in the water column (f_w) as a function of the fugacity in the atmosphere (f_a) for all simultaneous air and water samples for TTCE, BENZ, and TOL. Open symbols represent samples from European continental origin (cont.), and black symbols represent samples from non-European continental origin (noncont.).

fluxes varying between 0.6 (CCl_4) and $52.7 \mu\text{g m}^{-2} \text{d}^{-1}$ (CHCl_3). So by extrapolation it is found that, over a 1-year period, 10 (CCl_4) to 885 tons (CHCl_3) is emitted into the atmosphere in the southeastern area of the North Sea ($46\,000 \text{ km}^2$) (1), which is only 6.2% of the total North Sea.

In a steady state, the mean residence time of the VOCs can be calculated from

$$A d \frac{dC_w}{dt} = -N \quad (13)$$

where A is the surface area (m^2) and d is the water depth (m). So using eq 10 and writing C_w in terms of fugacity, one obtains

$$df_w = \frac{K_w}{d} \Delta f dt \quad (14)$$

with $\Delta f = f_w - f_a$ being the driving force for transfer. So the mean residence time $t_{1/2}$ is calculated in a steady state as

$$t_{1/2} = \frac{0.5 f_w d}{K_w \Delta f} \quad (15)$$

Applying this approach on average concentration data for VOCs with mean K_w (0.56 – 0.65 m d^{-1}) and R [from 0.07 (CHCl_3) to 0.80 (OXYL)] data, the mean residence times for the near coastal locations D, E, and F (4–15 km offshore) and for the more remote locations A, B, and C (35–60 km offshore) with mean depths of respectively 11.3 and 30.7 m (34) were calculated. CHCs mean residence times were found to be from 9 to 16 and from 24 to 44 days for the near-coast and more offshore locations, respectively. Due to higher air to water fugacity ratios, mean residence times for all MAHs, except OXYL, were higher: 16–33 and 43–91 days for the respective types of locations. For OXYL, showing the highest mean R ratio (0.80), mean residence times were calculated as 103 and 281 days, respectively.

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