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<http://dx.doi.org/10.1016/j.watres.2011.10.032>

1,4-dichlorobenzene as an indicator of the health risk of volatile organic compounds in recycled water

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Screening health risk assessment of VOCs in recycled water

ABSTRACT

Characterisation of the concentrations and potential health risks of chemicals in recycled water is important if this source of water is to be safely used to supplement drinking water sources. This research was conducted to: (i) determine the concentration of volatile organic compounds (VOCs) in secondary treated effluent (STE) and, post reverse osmosis (RO) treatment and to; (ii) assess the health risk associated with VOCs for indirect potable reuse (IPR). Samples were examined pre and post-RO in one full-scale and one pilot plant in Perth, Western Australia. Risk quotients (RQ) were estimated by expressing the maximum and median concentration as a function of the health value. Of 61 VOCs analysed over a period of three years, twenty one (21) were detected in STE, with 1,4-dichlorobenzene (94%); tetrachloroethene (88%); carbon disulfide (81%) and; chloromethane (58%) most commonly detected. Median concentrations for these compounds in STE ranged from 0.81 µg/L for 1,4-dichlorobenzene to 0.02 µg/L for carbon disulfide. After RO, twenty six (26) VOCs were detected, of which 1,4-dichlorobenzene (89%); acrylonitrile (83%) chloromethane (63%) and carbon disulfide (40%) were the more frequently detected. RQ(max) were all below health values in the STE and after RO. Median removal efficiency for RO was variable, ranging from -77% (dichlorodifluoromethane) to 91.2% (tetrachloroethene). The results indicate that despite the detection of VOCs in STE and after RO, their human health impact in IPR is negligible due to the low concentrations detected. The results indicate that 1,4-dichlorobenzene is a potential chemical indicator for assessment of VOCs in IPR using RO treatment.

Keywords: water recycling, water quality, organic pollutants, indirect potable reuse, volatile organic compounds, reverse osmosis

1. INTRODUCTION

Volatile organic compounds (VOCs) are organic chemicals that have a relatively low boiling point (≤ 250 °C measured at a standard atmospheric pressure of 101.3 kPa) and high vapor pressure relative to their water solubility. This class of chemicals therefore easily volatilize from water to air at room temperatures and enter the atmosphere upon contact with an air-water interface. Substances that are included in the VOC category are: aliphatic hydrocarbons (i.e. hexane), aromatic hydrocarbons (i.e. benzene, toluene and the xylenes), halogenated hydrocarbons (i.e. tetrachloroethene) and oxygenated compounds (i.e. acetone and similar ketones).

VOCs are widely used and comprise an important group of environmental contaminants. They are produced in large volumes and are associated with numerous products and applications, including household cleaners, fuel additives, and commercial and industrial solvents. VOCs dissolve many other substances and are used as cleaning and liquefying agents in fuels, degreasers, adhesives, solvents, polishes, cosmetics, refrigerants, drugs, and dry cleaning solutions (Zogorski et al. 2006). VOCs may be emitted from fabrics, carpets, fibreboard, plastic products, glues, solvents, household cleaners, printed material, methylated spirits, paints and

paint products (such as thinners or varnishes), disinfectants, cosmetics, degreasing products, and fuels. They are hence discharged to wastewater treatment plants (WWTP) from a large number of sources including commercial enterprises, industries, and residential households.

VOCs have been detected in many water types, including secondary treated effluent (STE). Aliphatic hydrocarbons, aromatic hydrocarbons, halogenated volatiles and dimethyl disulfide account for approximately 70% of all VOCs detected in municipal STE (Koe and Shen 1997). Although VOCs concentrations in raw wastewater may range from 1-150 µg/L, atmospheric emissions during treatment generally lead to significantly lower dissolved concentrations in STE (Atasoy E et al. 2004, Battistoni et al. 2007). Adsorption and biodegradation can reduce the concentration of VOCs in WWTPs. VOC release to the atmosphere during collection and in particular during aeration treatment is considered the most important method of removal of VOCs from STE (Fatone et al. 2011). The aeration that occurs during wastewater treatment and during many sludge treatment processes can achieve more than 90% removal of the VOCs concentration in raw wastewater (NRC 1996). For example, Wu et al (2002) reported a 96% decrease in total VOCs in a WWTP during exposure to the atmosphere via air stripping (Wu et al. 2002).

In some circumstances, VOCs may also be found in public drinking water supplies as a result of spills, discharges, atmospheric deposition or leaching from contaminated soils. Tetrachloroethylene, trichloroethene, 1,1-dichloroethene and benzene are examples of VOCs that are occasionally detected (Williams et al. 2002). Industrial discharges may lead to the release of VOCs into groundwater (along with gasoline oxygenates). For example, eighteen (18) of eighty-eight (88) VOCs were detected in twenty eight (28) wells sampled in the San Diego Groundwater Ambient Monitoring and Assessment study (Wright et al. 2005). Groundwater contamination with non-aqueous phase liquids, such as chlorinated solvents and petrol hydrocarbons, may pose a health risk if used as a drinking water source as they can be difficult to remove by treatment (Patterson et al. 1993).

The presence of VOCs in drinking water is of concern because some of these compounds have adverse health effects, including potential carcinogenesis, and because they can change the taste and odour of drinking water. The health impact of VOCs varies greatly from those that are highly toxic, to those with no known health effect. As with other organic chemicals, the extent and nature of the health effect will depend on the level of exposure and length of exposure. Some VOCs may adversely affect the liver, kidneys, spleen, and stomach, as well as the nervous, circulatory, reproductive, immune, cardiovascular, and respiratory systems. Some VOCs may affect cognitive abilities, balance, and coordination. At high levels of exposure, VOCs can cause central nervous system depression (Boyes et al. 2000, Brouwer et al. 2005, Herpin et al. 2009) and can be irritating upon contact with the skin, to mucous membranes of the eyes or to the mucous membranes if inhaled (Toccalino et al. 2006, WHO 2006). Acute symptoms after exposure to some VOCs (mainly from inhalation) include headaches, dizziness, visual disorders, and memory impairment. The chronic health effects to the general public from ingestion of VOCs at low concentrations in drinking water are less well understood but health values are well above offensive taste/odour thresholds and contain significant safety margins.

1.1 Regulatory Framework

VOCs comprise almost half of the 129 priority pollutants designated by the US EPA for limitation or prevention of introduction to water (U.S. EPA 1994), and some are also included in the European Commission priority pollutant lists. The EU adopted decision No 2455/2001/EC, which established a list of 33 priority substances in the field of water policy, include the following VOCs: benzene, C₁₀₋₁₃-chloroalkanes, 1,2-dichloroethane, dichloromethane, hexachlorobutadiene, trichlorobenzenes and trichloromethane (European Commission 1998)

In Australia, the National Industrial Chemical Notification and Assessment Scheme (NICNAS) is the federal agency assessing the human health risk of industrial chemicals including VOCs introduced into Australia. The assessment reports include hazard, exposure assessments and risk characterisation for occupational health and safety, environment and public health. The reports are available on the web and are classified as (i) new chemicals; (ii) priority existing chemicals; and (iii) other assessments (<http://www.nicnas.gov.au/Publications/CAR.asp>). National guidelines for sewerage systems - in particular those pertaining to (i) Effluent Management and (ii) Acceptance of Trade Waste (Industrial Waste) - provide a framework for sewerage authorities responsible for the management, monitoring, disposal and implementation of trade waste management programs.

Regulations exist for levels of VOCs in various contexts, such as water systems (drinking water, sewage discharges and stormwater disposal), occupational settings and air emissions. Australian Federal and State regulations often limit the quantity of VOCs that are emitted from sources such as industrial facilities, WWTPs and landfills. In Western Australia, the Department of Environment and Conservation regulates the level of contaminants allowable in wastewater streams under the Environmental Protection Act 1986 and may prescribe specific license conditions for VOCs, depending on the type of industry (NWC 2011). Examples of compounds that have to be reduced or removed from industrial facilities before discharge to sewers include benzene, trichlorethene, vinyl chloride and xylenes. Steam or air stripping, carbon adsorption and solvent extraction are all methods used for removing VOCs from wastewater before secondary treatment for compliance with regulatory requirements.

Regulatory agencies and institutions set drinking water values for VOCs based on toxicological and epidemiological assessments. For the majority of VOCs that are assumed to be non-carcinogenic, it is hypothesised that there is a threshold dose below which no adverse health effects will occur. Consequently, drinking water guidelines are calculated based on tolerable daily intake (TDI) values. The TDI values are derived from toxicological studies conducted in animals and epidemiological data when available. Some VOCs are known or suspected carcinogens. For those VOCs classed as carcinogenic (without a threshold dose), guideline values are derived using mathematical models that combine toxicological data with the concept of acceptable levels of risk for lifetime consumption. The WHO guideline values are derived using an acceptable level of risk of one in a thousand excess cancers attributable to a particular VOC consumption at the guideline concentration (WHO 2006). For the Australian Drinking Water Guidelines (ADWG), the acceptable level of risk is mainly based on one in a million excess cancers (ADWG 2011). In many cases the toxicological data used is the same but the assumptions used to calculate the health value varies. For example, the Canadian standard for 1,4-dichlorobenzene is 5 µg/L (Canadian Drinking Water Guidelines 2010) while the regulatory value for: USEPA is 75 µg/L (U.S. EPA 2011); WHO is 300 µg/L (WHO 2006) and for Australia is 40 µg/L (ADWG 2011)

The work presented in this paper is part of a larger project investigating the effectiveness of microfiltration/reverse osmosis (MF/RO) to treat STE for indirect potable reuse (IPR), a key water conservation strategy for Western Australia (DOHWA 2009). Lack of knowledge of health and environmental risks associated with chemicals and their removal by advanced treatment processes such as reverse osmosis (RO) has been major barriers preventing establishment of large reuse schemes in Australia. In this paper we evaluate the range and levels of VOCs at major points in the recycled water stream, including characterisation of STE and post-RO water for 61 VOCs and to assess the health risks associated with VOCs for IPR with post-RO water. As well as providing information on the efficacy of RO to remove specific VOCs, these results also provide the most extensive analysis of VOCs in treated wastewater in Australia published to date.

2. METHODS

2.1 Sample Sites

Six (6) sampling events were conducted from November 2006 to June 2008 (Table 1), with an overall total of 32 sampling days. Typically a single sampling event consisted of between 4 and 6 sampling trips over a week, with sampling focused on STE or and post-RO water. However, on a number of occasions, post-MF water was also undertaken. During membrane treatment, wastewater undergoes chloramination before MF to prevent RO membrane fouling and samples of post-MF water were analysed to determine the effect of chloramination during the MF/RO process. Grab STE samples represent the three major WWTPs in Perth and were taken directly from Beenyup WWTP and Subiaco WWTP and at the influent stream of the Kwinana Water Reclamation Plant (KWRP) for Woodman Point WWTP. Samples post-MF and post-RO were collected from two advanced treatment plants at KWRP and Beenyup Pilot Plant (BPP) in order to characterise water quality through the membrane treatment process. Details of each have been previously published (DOHWA 2009) but but briefly, KWRP treats secondary treated wastewater from Woodman Point WWTP by MF/RO to produce approximately 16 ML/day of general process water for neighbouring industrial facilities, reducing Perth's total demand for scheme water by about 2%. The BPP treats a small volume of STE (approximately 100 kL/day) from Beenyup WWTP by MF/RO and is the first stage of a larger project investigating indirect potable reuse of Beenyup STE. The BPP was commissioned after the May/June 2007 sampling event (sampling event 2 in Table 1). Both plants are owned by the Water Corporation of Western Australia. Woodman Point WWTP receives wastewater primarily from residential areas, but also has about 6% content from industrial facilities (DOHWA 2009), while Beenyup WWTP has a sewer catchment that is mainly residential in nature.

Grab samples were also collected from groundwater (GW) during sampling events 2 and 4. The groundwater in this context corresponds to the raw drinking water source. Standard protocols were used to ensure adequate sample preparation, preservation and transportation to the laboratory. Laboratory blanks, trip and field blanks were also analysed and constituted about one third of the samples analysed.

2.2 Analysis of VOCs

The selection of VOCs was based on their risk profiles and factors. The following criteria were used to guide analytes inclusion in the target list: (i) the VOC is currently or has been registered for use in Australia; (ii) there is a high likelihood of the VOC being detected in wastewater based on known chemical and physical properties; (iii) the VOC has previously been detected in natural waters or wastewater; (iv) there were public perceptions that the chemical may pose a possible public health hazard; and v) the VOC is listed in the ADWG (2004) or other international regulatory agencies as regulated or as part of any contaminant candidate list.

All VOCs except acrolein, acrylonitrile and methyl tertiary butyl ether (MTBE) were measured by purge and trap GC-MS. Acrolein, acrylonitrile, MTBE were extracted and pre-concentrated by headspace solid-phase microextraction (SPME) before GC-MS analysis. Quantification was performed by mass spectrometry (MS) with electron ionisation (EI), with peak identification and calculation of recovery was aided by inclusion of surrogate standards. Limits of detection were determined for every analytical run and were calculated using the standard deviation of replicate analyses of a standard solution of appropriate concentration (typically 0.05-0.1 µg/L). Standard deviations were then converted to 95% confidence intervals using the student's t-test.

Relative standard uncertainties were calculated using an uncertainty budget that incorporated precision, calibration standard preparation, sample volume, and linear regression of the calibration curve. Sample homogeneity was considered a negligible source of uncertainty. Acrolein and acrylonitrile were not validated to the same extent as other VOCs because they were only analysed during sampling event 3. The VOCs analysed, standard relative uncertainty at 0.5 µg/L, and average LODs are presented in Tables 2 and 3.

2.3 Data Analysis

Unlike other chemical classes of compounds (e.g. dioxins), there is no common toxicological mechanism for VOCs, and therefore the potential human health risk was evaluated for individual compounds. Risk quotients (RQ) were estimated by expressing the maximum and median concentration in STE as a function of the health value for detected VOCs. For VOCs without detections in STE, RQs were calculated as the ratio between the LOD and the health value as a worst case scenario. A three tiered screening health risk assessment approach was used for the derivation of the health values. The basis for the tool has been discussed and applied in previous publications (Rodriguez et al. 2007a, Rodriguez et al. 2007b). Under this system, VOCs were allocated to “tier 1 (regulated contaminants)”; “tier 2 (unregulated contaminants with toxicity information)” or “tier 3 Threshold of Toxicological Concern (unregulated contaminants with toxicity information)”. For VOCs in tier 1, the order or priority for setting the health benchmark values was the ADWG (2011) (ADWG 2011), the ADWG (2004) (ADWG 2004), WHO guidelines including the 2nd addendum to the 3rd edition published in 2006 (WHO 2006), the Drinking water standards and health advisories from the U.S. EPA (U.S. EPA 2011) and the

California Drinking Water Notification Levels and Response Levels (CDPH 2010), based on the methodology previously described (Rodriguez et al. 2007b).

Data were analysed in Stata version 10 (Stata Corp 2007). Comparison of median concentrations was performed using non-parametric tests. For median comparison between KWRP and BPP the Mann-Whitney test was used, while the Kruskal Wallis X^2 test was used for comparison of median values of three or more groups. Results are reported at a significance level of 5% ($p < 0.05$).

3. RESULTS

A total of 61 VOCs were analysed in at least one sampling event. A total of 4,326 measurements were analysed for VOCs excluding QA/QC samples. The distribution of sampling by event and location is presented in Table 1.

3.1 Secondary treated effluent (STE)

Twenty one (21) VOCs (34% of the total) were detected in STE (Table 2). The most frequently detected VOC was 1,4-dichlorobenzene (93.9% of STE samples), followed by tetrachloroethene (87.9%), carbon disulfide (81.2%) and chloromethane (57.6%). Of the 21 VOCs detected, fourteen (14; 67%) were detected in less than 30% of the samples analysed, indicating that the presence of the compounds in STE is not consistent. Median concentrations for these compounds were dominated by non-detects, reported as LOD. Seven (7) VOCs (i.e. 1,4-dichlorobenzene, cis-1,2-dichloroethene, carbon disulfide, chloromethane, tetrachloroethene, acrylonitrile and trichloroethene) had a percentage of detections greater than 30% across all samples (Table 2). For these compounds, median concentrations ranged from 0.81 $\mu\text{g/L}$ for 1,4-dichlorobenzene to 0.02 $\mu\text{g/L}$ for carbon disulphide.

Comparison for the 7 VOCs with percentage detections greater than 30% showed that median concentrations were generally higher for influent STE from KWRP compared to BPP (Mann-Whitney $p = 0.0001$). For example, the median concentration of chloromethane at KWRP STE influent was double the median concentration at BPP STE influent (KWRP median = 0.12 $\mu\text{g/L}$; BPP median = 0.06 $\mu\text{g/L}$). The median concentration of tetrachloroethene in the STE entering KWRP was 5.4 times higher than the corresponding at BPP (KWRP median = 2.2 $\mu\text{g/L}$; BPP median = 0.41 $\mu\text{g/L}$). For 4 VOCs the concentrations in KWRP STE influent were statistically higher than BPP STE influent (Figure 1), i.e. 1,2-dichloroethene cis (Mann-Whitney test, $p = 0.001$), chloromethane ($p = 0.004$), tetrachloroethene ($p = 0.02$) and trichloroethene ($p = 0.001$). For 1,4-dichlorobenzene and acrylonitrile, the median concentrations were slightly higher at BPP STE influent but the differences were not statistically significant. Samples from Subiaco WWTP were not included in the comparison as fewer samples were taken at this location compared to KWRP and BPP.

Seasonal comparison of median VOC concentrations is presented in Figure 2. Again comparison is only made for compounds with percentage detections greater than 30% (i.e. 1,4-

dichlorobenzene, cis-1,2-dichloroethene, carbon disulfide, chloromethane, tetrachloroethene and trichloroethene). , except for acrylonitrile which was not included because it was only analysed during sampling event 3 (n=6, Table 2). Overall median VOC concentrations were higher in spring (0.125 µg/L) and winter (0.12 µg/L) than in summer (0.025 µg/L) and autumn (0.022 µg/L). These differences were statistically significant (Kruskal Wallis X^2 p=0.0001). The VOCs: 1,4-dichlorobenzene, tetrachloroethene, and trichloroethene all had highest median concentrations in spring, whereas the highest median concentrations for cis-1,2-dichloroethene and chloromethane were equal in spring and winter. The highest median concentration for carbon disulphide was recorded in winter, although it should be noted that it was not analysed in spring sampling events (Table 1).

3.2 Post-MF water

Twenty seven (27) VOCs were detected in post-MF samples, a higher number than in STE samples (21). Sixteen (16) of the 27 VOCs in the post-MF samples were also detected in STE (Table 2). Of the 27 VOCs detected in post-MF water, 18 were detected at KWRP only (Figure 5) and 1 (i.e. 1,3-dichloropropene) was detected at BPP only. Eight (8) VOCs were detected at both locations: 1,2-dichlorobenzene, 1,4-dichlorobenzene, benzene, carbon disulfide, chloromethane, tetrachloroethene, toluene and o-xylene.

3.3 Post-RO water

A total of 26 VOCs (43%) were detected in post-RO water and 18 of these VOCs were also detected in STE (Table 2). The most commonly detected VOC was 1,4-dichlorobenzene (89.9% detections) followed by acrylonitrile (83.3%), chloromethane (62.9%) and carbon disulfide (40.0%), with respective median concentrations of 0.19 µg/L, 0.13 µg/L, 0.09 µg/L, and 0.02 µg/L. Five VOCs (i.e. ethylbenzene, naphthalene, n-butylbenzene, m-xylene and p-xylene) were detected in post-RO water and post-MF water but not in STE. Three VOCs were only detected in post-RO water (i.e. 1,2,3-trichlorobenzene, chlorobenzene and tert butylbenzene), although all with a percentage of detection below 11%. The percentage detection for all VOCs detected in post-RO water but not in STE was below 10% except for p-xylene (15.4%) (Table 2).

3.4 Groundwater

Three (3) VOCs (i.e. 1,4-dichlorobenzene, benzene and toluene) were detected in groundwater. 1,4-dichlorobenzene (0.005 µg/L) was detected once in a sample taken from bore line A during sampling event 4 (January 2008). A replicate sample from bore line A and a sample from bore line B taken the same day were below the LOD (0.003 µg/L). Benzene was also detected above LOD (0.04 µg/L) in all groundwater samples taken during sampling event 4. Two replicate samples from bore line A were 0.08 µg/L and 0.13 µg/L, while the concentration in the single bore line B sample was 0.1 µg/L. Toluene (0.54 µg/L) was detected once in a sample from bore line B during sampling event 2. The toluene concentration of bore line A sample taken on the same day was below LOD (0.13 µg/L).

3.5 Screening health risk assessment

Of 61 VOCs analysed, 34 (55.7%) were classified in tier 1, 18 (29.5%) were classified in tier 2 and the remaining 9 (14.8%) were classified in tier 3. The list of VOCs analysed, the corresponding tier, health value and calculated RQs are presented in Tables 2 and 3.

The VOCs were classified according to the IARC cancer classification and the U.S. EPA cancer classification. Almost half of the VOCs analysed had not been evaluated (27, 44.6%). Of the 34 VOCs evaluated: two (2) are classified as carcinogenic to humans (benzene and vinyl chloride); four (4) are classified as probably carcinogenic to humans (tetrachloroethene, trichloroethene, ethylene dibromide and 1,2,3-trichloropropane); ten (10) are classified as possible carcinogenic to humans (group 2B) and; eighteen (18) are unclassifiable as to carcinogenicity in humans (group 3) Figure 3. No significant differences were observed in the IARC cancer classification distribution of the detected VOCs. Similarly, of the 61 VOCs analysed, 16 (26.2%) had not been evaluated by the US EPA. Two (2) VOCs are classified as human carcinogens, seven (7) are classified as probable human carcinogens; seven (7) are classified as possible human carcinogens, and sixteen (16) are not classifiable as to human carcinogens.

The RQ for the VOCs detected in any STE, post-MF or post-RO sample are presented in Table 2. In STE samples, both RQ(max) and RQ(median) were always below 1. Most calculated RQ(max) were between one and three orders of magnitude below 1, whereas all RQ(median) were between one and four orders of magnitude below 1. However, RQ(max) was only slightly below 1 for chloroethane (RQ=0.8); tetrachloroethene (RQ=0.2); MTBE (RQ=0.13) and; benzene (RQ=0.1). RQs for VOCs detected in post-MF water but not in STE or post-RO water (Table 2) were all below 1 with the highest RQ(max) = 0.3 for 2-propyltoluene. In post-RO water, both RQ(max) and RQ(median) were again consistently below 1. The highest RQ(max) was for benzene (0.14), with all other values between one and three orders of magnitude below 1. For RQ(median), all values were between one and four orders of magnitude below 1. The results indicate that chemical concentrations measured in post-RO water are not of human-health concern.

A total of 26 VOCs were not detected in any STE, post-MF or post-RO samples (Table 3). RQs for undetected VOCs were calculated using the average LOD as a worst case scenario. For twenty (20) of the undetected VOCs the calculated RQs were between one and four orders of magnitude below 1. For the other 6 undetected VOCs, RQs were slightly higher but all remained below 1 ranging from 0.11 (1,3-Dichloropropane) to 0.32 (2,2-dichloropropane). The human health risk from these VOCs is therefore estimated to be negligible.

This screening health risk assessment is based on VOCs concentrations in water for human consumption. However, for a comprehensive risk assessment, it is necessary to consider other routes of exposure, including inhalation and dermal uptake. In the Perth context, VOC concentrations in post-RO water are very low and any potential human risk from inhalation,

dermal contact and ingestion will be further minimised by the retention time of the injected recycled water into the confined aquifer. Consequently, no human health risk is anticipated at the VOCs concentrations detected in the post-RO water. With respect to other environmental sources, it is likely that diet accounts for some VOC exposure (Fleming-Jones and Smith 2003), with inhalation accounting for a larger portion of human intake through VOCs emitted by cigarette smoke, vehicles, household products and industrial pollution. Consequently, risks to human health from VOCs in recycled water for IPR are likely to be negligible with negligible impact on public health compared to other sources of exposure.

4. DISCUSSION

4.1 VOC Concentrations in STE

A total of 21 VOCs were detected in STE, of which 14 (67%) were detected in less than 30% of the samples analysed. The low concentration and inconsistent occurrence of VOCs in STE in our study may indicate that (i) adequate industrial waste acceptance criteria are in place to limit or prohibit discharge of substances from commercial or industrial premises in Perth, and/or; (ii) WWTPs are able to effectively remove VOCs from raw wastewater. The concentration of VOCs detected in STE depends on the relative importance of removal processes during the wastewater treatment, such as adsorption onto sludge, chemical transformation, volatilization, and biodegradation. The results are consistent with previous studies showing low concentrations of VOCs in STE attributable to significant reductions during municipal wastewater treatment (more than 90% removal) (Wu et al. 2002).

Significant differences in the median concentrations of VOCs were found between the STE influent of KWRP and BPP. This may be related to the differences in level of contamination of the wastewater in the catchments and geographical variability in industrial activities. The higher VOCs concentrations seen in STE samples at KWRP compared to BPP may be related to the fact that KWRP is on the site of an oil refinery. This finding reinforces the importance of wastewater characterisation for projects considering IPR, given the different nature of industry, trade waste agreements/regulations, sewer arrangements and WWTP process in place. Our results are consistent with other studies indicating that the VOCs detected in a WWTP are closely related to the industrial activities in the catchment. For example Cheng et al (2008) found that the more common VOCs detected in STE were as follows: acetone, acrylonitrile, methylene chloride, and chloroform for the petrochemical districts; acetone, chloroform, and toluene for the science-based districts; and chlorinated and aromatic hydrocarbons for the multiple industrial districts (Cheng et al. 2008). In contrast Fatone et al. (2011) found that BTEX compounds (excluding benzene) to be the most commonly detected VOCs in five municipal WWTP, assumed to result from vehicle emissions.

Seasonal differences in some VOCs concentrations were also observed, with higher concentrations observed in winter and spring compared to summer and autumn. VOCs are more likely to be stable and detectable in cold water because warm temperatures can cause VOCs to volatilize (Metz et al. 2007) and to more readily undergo degradation by the activated sludge process (Martínez et al. 2006). This seasonality was consistent when duplicate seasonal sampling

was undertaken in summer and winter. The results also correspond with findings from air pollution studies that report higher concentrations of VOCs in air during summer.

4.2 VOC Concentrations in Groundwater

Three VOCs (i.e. 1,4-dichlorobenzene, benzene and toluene) were detected in groundwater, marginally above the LOD. Toluene and benzene may indicate potential VOC contamination of groundwater, as previously reported in association with landfills and leaking underground petrol storage tanks (Zogorski et al. 2006). Given the limited number of samples and low concentrations detected, further investigation is required to confirm the presence of these compounds in Perth's groundwater. VOCs have been frequently detected in shallow ground water beneath urban areas (up to 90% of samples) (Hamilton et al. 2004). Samples taken during this study were a mixture of groundwater from shallow aquifers and deep, confined aquifers. In general, deep aquifers are less vulnerable than shallow aquifers to anthropogenic contaminants that originate on or near the land surface. In other locations, VOCs contamination has been observed in public wells which draw on proportionately large volumes of groundwater situated below developed areas (Zogorski et al. 2006).

However, in Western Australia, all public drinking water bores are protected by catchment protection reserves.

4.3 The effect of MF/RO treatment on VOC concentration

In both the BPP and KWRP, wastewater undergoes chloramination before MF to prevent RO membrane fouling. Samples of post-MF water were therefore analysed to determine the effect of chloramination during the MF/RO process. Paired wastewater, post-MF and post-RO samples were taken on 6 occasions at KWRP (1 in sampling event 1, 3 in sampling event 2, 1 in sampling event 3 and 1 in sampling event 6) and on 3 occasions at BPP (sampling events 3, 4 and 6).

At KWRP, there were 21 analytes for which the highest median concentration was measured in a post-MF sample: chloromethane, trichlorofluoromethane (freon 11), carbon disulphide, cis-1,2-dichloroethene, trichloroethene, benzene, toluene, ethyl benzene, o-xylene, m-xylene, p-xylene, styrene, 1,3,5-trimethylbenzene, tert-butyl benzene, 1,2,4-trimethylbenzene 1,3-dichlorobenzene, 2-propyltoluene, p-isopropyl toluene, 1,2-dichlorobenzene, n-butyl benzene, and naphthalene. Although the percentage detections for some of these analytes were low, 11 were present in more than 50% of post-MF samples: chloromethane (100%), cis-1,2-dichloroethene (83%), toluene (83%), ethyl benzene (100%), o-xylene (100%), m-xylene (100%), p-xylene (100%), styrene (67%), 1,3,5-trimethylbenzene (83%), 1,2,4-trimethylbenzene (100%), and naphthalene (83%).

During this research project, chloramination was found to increase the concentration of some disinfection by-products (DBPs) during MF/RO treatment, particularly the halomethanes (DOHWA 2009, Linge et al. 2011). Chloromethane is considered a disinfection by-product (Krasner et al. 2006) solvent and would not be expected to be formed by disinfection. All of the other nine VOCs frequently detected in post-MF samples are aromatic compounds associated with gasoline or diesel exhaust (Elbir et al. 2007, Watson et al. 2001) or with oil refinery emissions (Chen et al. 2006, Scheff and Wadden 1993). The KWRP MF/RO plant is located on the site of an oil refinery that produces petrol, diesel, liquefied petroleum gas, aviation gasoline, jet fuel and bitumen and it is likely that trace concentrations of associated compounds would be

found in water samples from KWRP. The low concentrations measured in post-RO water and field blanks compared to post-MF water suggests that this contamination did not occur during sampling, but most likely occurred during the MF treatment where the water is exposed to the atmosphere for about 25 minutes. A number of the tanks also have air vents that may enable some exposure to the atmosphere both before MF and after RO of up to an hour, although the vents are less likely to be a significant source of exposure compared with the open tanks.

At BPP, there were only 4 VOCs for which the highest median concentration was measured in a post-MF sample: i.e. carbon disulphide (66%), toluene (100%), 1,3-dichloropropene (33%), and 1,2-dichlorobenzene (66%). These compounds are unlikely to form through chlorination or chloramination. However, they do not show the characteristic fingerprint of petroleum-based contamination and the source of these VOCs is not obvious at this time.

4.4 Treatment performance

Overall treatment efficiency was calculated as a proportion of removal, comparing STE and post-RO samples that were matched for plant and date. For those parameters reported below LOD after RO, the efficiency was calculated assuming a concentration equal to half the LOD. Very high variability in the removal of VOCs was observed, as illustrated in Figure 4. For ten (10) of the twenty one (21) VOCs detected in STE, the median removal efficiency was above 70%. The median removal efficiency ranged from -77.0% for dichlorodifluoromethane to 91.2% for tetrachloroethene.

For 17 samples, corresponding to 6 VOCs (1,4-dichlorobenzene=1 sample, benzene=4, carbon disulfide=3, chloromethane=7, dichlorodifluoromethane=1, o-xylene=1), the concentrations in post-RO samples were higher than their paired STE samples. For 10 (59%) of these paired samples, the concentration in post-RO water was not statistically different from the STE: the difference was within the uncertainty of the analytical method and therefore calculation of removal efficiency using these data is inconclusive. Differences were seen (outside of the limits of uncertainty) for carbon disulphide (1 sample), chloromethane (4 samples), dichlorodifluoromethane (1 sample), and o-xylene (1 sample). As discussed earlier, elevated concentrations of carbon disulphide and o-xylene occurred in post-MF samples and therefore the increased concentrations in post-RO samples may be a result of contamination. Chloromethane was also elevated in post-MF samples.

Given the apparent increase in some VOCs in post-MF samples, the treatment efficiency of RO alone was determined using paired post-MF and post-RO samples by plant (Figure 6). Calculations confirmed that the degree of RO treatment efficiency was higher than overall MF/RO plant treatment efficiency for all VOCs detected in STE with the exception of chloroethane, tetrachloroethene, toluene and dichlorodifluoromethane. Furthermore, by using post-MF data, treatment efficiency could be calculated for 10 additional VOCs, which were measured in post-MF samples but were not present in STE. As shown in Figure 6, the majority of positive VOCs in post-MF water occurs at KWRP (n=26) compared to BPP (n=9). Variability in RO treatment efficiency (calculated using post-MF and post-RO data) as represented by standard deviation, fell slightly but remained relatively high, although this may relate to the smaller number of paired samples available for analysis.

The rejection of VOCs in a range of different RO membranes has been reported as highly variable. For some VOCs (1,1,1-trichloroethane, carbon tetrachloride, p-, m- and o-xylenes,

tetrachloroethylene, 1,2-dichlorobenzene), rejection has been reported as higher than 90% (Agenson et al. 2003), but for others rejection has been reported as much lower (6-54% for benzene). Using paired post-MF and post-RO samples, 56% of analytes in this study had rejection efficiency greater than 80%, while 37% had rejection efficiency greater than 90%. Lower median rejection was associated with benzene (56%), bromomethane (48%) and styrene (63%). It has been found that rejection of VOCs is influenced by solute size, branching of functional groups and K_{ow} (Agenson et al. 2003). VOCs with poorer rejection usually have smaller molecular width and length, and lower K_{ow} while VOCs are not highly hydrophobic ($\log K_{ow} < 3$), K_{ow} has been found to influence rejection, which suggests that there is some degree of interaction between the solute and the membrane.

4.5 Identification of Treatment Performance Indicator

The use of chemical indicators in recycled water has been proposed for occurrence monitoring and for assessing treatment process performance assessment (Drewes et al. 2008, Benotti et al. 2009, Dickenson et al. 2011). A treatment performance indicator is an individual chemical occurring at quantifiable level that represents a family of trace constituents with certain physicochemical and biodegradable characteristics that are relevant to fate and transport during treatment, in this case RO. A treatment performance indicator should provide a conservative assessment of removal of represented parameters, and should be sensitive to minor changes in RO treatment performance.

The criteria for selection of a Treatment Performance Indicator are:

- Quantifiable using an established and preferably accredited analytical method;
- Frequently detected in feed water, preferably 100% detections;
- Present in feed water at significant concentrations; generally greater than five times LOD;

The selection of a chemical indicator for VOCs is challenging given the diversity of compounds in this chemical group. However, it is neither practical nor feasible to assess for all potential VOCs present in recycled water during routine monitoring. In our study, 1,4-dichlorobenzene was identified as a potential treatment performance indicator for assessment of VOCs in IPR using RO treatment (Blair et al. 2010). 1,4-dichlorobenzene was detected in almost 94% of the STE samples and in almost 89% of the post-RO water samples, and median treatment efficiency by MF/RO treatment was 80%. 1,4-dichlorobenzene has been reported as one of the less biodegradable VOCs in wastewater (Koe and Shen 1997) and has a long history of domestic use in toilet products, moth repellents, and mildew control agents (Aronson et al. 2007, NICNAS 2000).

The relevance of 1,4-dichlorobenzene as a chemical indicator of VOCs will be further validated during the Groundwater Replenishment Trial (GWRT) (DOHWA 2009). During the three-year trial, 8 ML/day of STE from the Beenyup WWTP will be treated by MF/RO and UV disinfection before injection into a confined aquifer. If successful, this approach could significantly reduce the analytical cost and complexity of monitoring water treatment systems performance for removal of VOCs.

5. CONCLUSIONS

The screening health risk assessment indicates that the individual VOCs measured in recycled water have a low potential to affect humans from long-term consumption after RO treatment. Detection of VOCs in STE can occur as a result of the widespread use of these compounds. However, the impact on potable supplies through augmentation with recycled water treated by MF/RO is likely to be negligible at the concentrations observed in Perth.

Calculated MF/RO treatment removal was variable, with some concentrations in post-RO water higher than in the preceding STE. For some VOCs, this may be due to uncertainty in the analytical method. However, for others it is attributed to industrial contamination during the MF/RO process. For most VOCs, RO treatment efficiency was higher than overall MF/RO treatment efficiency, however more analysis of VOCs before and after RO treatment is recommended to better characterise the RO treatment variability.

Management of risks in IPR is dependent on advanced treatment technologies and comprehensive risk management approaches to ensure compliance with drinking water guidelines. Frequent monitoring of a treatment performance indicator such as 1,4-dichlorobenzene (in conjunction with the continuous online monitoring of critical control points) during the MF/RO treatment process is likely to be sufficient to ensure adequate removal of VOCs. If successful, this approach has the potential for significantly reducing the analytical costs and complexity of monitoring water treatment systems performance for removal of VOCs, and other chemical groups.

Acknowledgements: This research was conducted as part of the Premiers Collaborative Research Project (PCRP) a collaborative effort between Department of Health, Department of Water, Department of Environment & Conservation, Water Corporation of Western Australia, The University of Western Australia, Curtin University of Technology, Chemistry Centre WA and the National Measurement Institute (NMI). State government funding was provided by the Office of Science & Innovation.

REFERENCES

- ADWG (2004) Australian Drinking Water Guidelines, p. 615 p, National Health and Medical Research Council and Natural Resource Management Ministerial Council, Artarmon, NSW.
- ADWG (2011) Australian Drinking Water Guidelines, National Health and Medical Research Council and Natural Resource Management Ministerial Council, Canberra.
- Agenson, K., Oh, J.-I. and Urase, T. (2003) Retention of a wide variety of organic pollutants by different nanofiltration/reverse osmosis membranes: controlling parameters of process. *J membr sci* 225(1-2), 91-103.
- Aronson, D., Bosch, S., Gray, D.A., Howard, P. and Guiney, P. (2007) A Comparative Human Health Risk Assessment of p-Dichlorobenzene-Based Toilet Rimblock Products Versus Fragrance/Surfactant-Based Alternatives *Journal of Toxicology and Environmental Health Part B: Critical Reviews* 10(7), 467-526(460)
- Atasoy E, Döğeroğlu T, Kara S. (2004) The estimation of NMVOC emissions from an urban-scale wastewater treatment plant. *Water Research* 38(14-15), 3265-3274.
- Battistoni, P., Cola, E., Fatone, F., Bolzonella, D. and Eusebi, A.L. (2007) Micropollutants Removal and Operating Strategies in Ultrafiltration Membrane Systems for Municipal Wastewater Treatment. *Industrial & Engineering Chemistry Research* 46(21), 6716-6723
- Benotti, M., Trenholm, R., Vanderford, B., Holady, J., Stanford, B. and Snyder, S. (2009) Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water. *Environ Sci Technol.* 43(3), 597-603.
- Blair, P., Linge, K., Rodriguez, C., Busetti, F., Drewes, J. and Turner, N. (2010) Development of the system to manage chemical risk during indirect potable reuse Desalination, P.W.R. (ed), WateReuse Association, Sydney.
- Boyes, W.K., Bushnell, P.J., Crofton, K.M., Evans, M. and Simmons, J.E. (2000) Neurotoxic and pharmacokinetic responses to trichloroethylene as a function of exposure scenario. *Environ Health Perspect* 108 Suppl 2, 317-322.
- Brouwer, D.H., de Pater, N.A., Zomer, C., Lurvink, M.W. and van Hemmen, J.J. (2005) An experimental study to investigate the feasibility to classify paints according to neurotoxicological risks: occupational air requirement (OAR) and indoor use of alkyd paints. *Ann Occup Hyg* 49(5), 443-451.
- Canadian Drinking Water Guidelines (2010) Guidelines for Canadian Drinking Water Quality, Federal-Provincial-Territorial Committee on Drinking Water, Ontario

- CDPH (2010) California Department of Public Health, Drinking Water Notification Levels and Response Levels, California
- Chen, C.-L., Shu, C.-M. and Fang, H.-Y. (2006) Location and Characterization of Emission Sources for Airborne Volatile Organic Compounds Inside a Refinery in Taiwan. *Environmental Monitoring and Assessment* 120, 487-498.
- Cheng, W.-H., Hsu, S.-K. and Chou, M.-S. (2008) Volatile organic compound emissions from wastewater treatment plants in Taiwan: Legal regulations and costs of control. *Journal of Environmental Management* 88(4), 1485-1494.
- Dickenson, E.R.V., Snyder, S.A., Sedlak, D.L. and Drewes, J.E. (2011) Indicator compounds for assessment of wastewater effluent contributions to flow and water quality. *Water Research* 45(3), 1199-1212.
- DOHWA (2009) Premier's Collaborative Research Program (2005-2008). Characterising Treated Wastewater For Drinking Purposes Following Reverse Osmosis Treatment, Department of Health, Western Australia (DOHWA), Perth, WA
- Drewes, J.E., Sedlak, D., Snyder, S. and Dickenson, E. (2008) Development of indicators and surrogates for chemical contaminant removal during wastewater treatment and reclamation, WaterReuse Foundation, Alexandria, VA.
- Elbir, T., Cetin, B., Cetin, E., Bayram, A. and Odabasi, M. (2007) Characterization of volatile organic compounds (VOCs) and their sources in the air of Izmir, Turkey. *Environ Monit Assess.* 133(1-3), 149-160.
- European Commission (1998) Guidelines of water intended for human consumption. Official Journal of the European Communities.
- Fatone, F., Di Fabio, S., Bolzonella, D. and Cecchi, F. (2011) Fate of aromatic hydrocarbons in Italian municipal wastewater systems: an overview of wastewater treatment using conventional activated-sludge processes (CASP) and membrane bioreactors (MBRs). *Water Res* 45(1), 93-104.
- Fleming-Jones, M.E. and Smith, R. (2003) Volatile Organic Compounds in Foods: A Five Year Study *Journal of Agriculture and Food Chemistry* 51, 8120-8127.
- Hamilton, P.A., Miller, T.L. and Myers, D.N. (2004) Water quality in the nation's streams and aquifers--overview of selected findings, 1991-2001, p. 20 p, U.S.Geological Survey,, Reston, Va.
- Herpin, G., Gargouri, I., Gauchard, G.C., Nisse, C., Khadhraoui, M., Elleuch, B., Zmirou-Navier, D. and Perrin, P.P. (2009) Effect of chronic and subchronic organic solvents exposure on balance control of workers in plant manufacturing adhesive materials. *Neurotox Res* 15(2), 179-186.

- Koe, L.C.C. and Shen, W. (1997) High Resolution GC - MS Analysis of VOCs in Wastewater and Sludge. *Environmental Monitoring and Assessment* 44(1), 549-561.
- Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R., Scilimenti, M.J., Onstad, G.D. and Alfred D. Thruston, J. (2006) Occurrence of a new generation of disinfection byproducts. *Environ Sci Technol* 40(23), 7175-7185.
- Linge, K.L., Blythe, J.W., Buseti, F., Blair, P. and Heitz, A. (2011) (in prep) Formation of halogenated disinfection by-products during wastewater recycling employing microfiltration and reverse osmosis. *Environmental Science & Technology*. . *Environmental Science & Technology*.
- Martínez, S.A., Rodríguez, M.G. and Morales, M.A. (2006) Stability Analysis of an Activated Sludge Bioreactor at a Petrochemical Plant at Different Temperatures *International Journal of Chemical Reactor Engineering* 3(A62).
- Metz, P.A., Delzer, G.C., Berndt, M.P., Crandall, C.A. and Toccalino, P.L. (2007) Anthropogenic organic compounds in ground water and finished water of community water systems in the northern Tampa Bay area, Florida, 2002–04, p. 48 p., U.S. Geological Survey, Reston, Virginia.
- NICNAS (2000) Summary: Priority Existing Chemical Assessment Reports. PEC No. 13. para-Dichlorobenzene. . Australia, C.o. (ed), Canberra.
- NRC (1996) Use of reclaimed water and sludge in food crop production, National Academic Press, Washington.
- NWC (2011) Environmental health management, Australian Government, National Water Commission, Canberra ACT
- Patterson, B.M., Pribac, F., Barber, C., Davis, G.B. and Gibbs, R. (1993) Biodegradation and retardation of PCE and BTEX compounds in aquifer material from Western Australia using large-scale columns. *Journal of Contaminant Hydrology* 14(3-4), 261-278.
- Rodriguez, C., Cook, A., Van Buynder, P., Devine, B. and Weinstein, P. (2007a) Screening health risk assessment of micropollutants for indirect potable reuse schemes: a three-tiered approach. *Water Sci Technol* 56(11), 35-42.
- Rodriguez, C., Weinstein, P., Cook, A., Devine, B. and Buynder, P.V. (2007b) A proposed approach for the assessment of chemicals in indirect potable reuse schemes. *J Toxicol Environ Health A* 70(19), 1654-1663.
- Scheff, P.A. and Wadden, R.A. (1993) Receptor modeling of volatile organic compounds. 1. Emission inventory and validation. *Environ. Sci. Technol.* 27(4), 617-625.
- Stata Corp (2007) Stata Statistical Software, SE ver. 10. Station, C. (ed), TX: StataCorp LP., Texas.

- Toccalino, P.L., Rowe, B.L. and Norman, J.E. (2006) Volatile organic compounds in the Nation's drinking-water supply wells - what findings may mean to human health, p. 4 p., U.S. Geological Survey, Sacramento, California.
- U.S. EPA (1994) Emerging technology report cross-flow pervaporation system for removal of VOCs from contaminated wastewater, p. 129, Risk Reduction Engineering Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, Ohio.
- U.S. EPA (2011) Drinking water standards and health advisories, Office of Water, U.S. Environmental Protection Agency, Washington, D.C
- WHO (2006) Guidelines for Drinking-water Quality - Incorporating First Addendum to Third Edition - Volume 1: Recommendations, World Health Organization, Geneva.
- Watson, J.G., Chow, J.C. and Fujita, E.M. (2001) Review of volatile organic compound source apportionment by chemical mass balance. *Atmospheric Environment* 35(9), 1567-1584.
- Williams, P., Benton, L., Warmerdam, J. and Sheehans, P. (2002) Comparative risk analysis of six volatile organic compounds in California drinking water. *Environ Sci Technol* 36(22), 4721-4728.
- Wright, M., Belitz, K. and Burton, C. (2005) California GAMA Program: Ground-water quality data in the San Diego drainages hydrogeologic province, p. 102 pages, U.S. GEOLOGICAL SURVEY, Sacramento, California.
- Wu, C., Lu, J. and Lo, J. (2002) Analysis of volatile organic compounds in wastewater during various stages of treatment for high-tech industries. *Chromatographia* 56(1), 91-98.
- Zogorski, J., Carter, J.M., Ivahnenko, T., Lapham, W.W., Moran, M.J., Rowe, B.L., Squillace, P.J. and Toccalino, P.L. (2006) Report on volatile organic compounds in the nation's ground water and drinking-water supply wells, p. 112 pages, U.S. Department of the Interior, U.S. Geological Survey, Reston, VA.

Table 1: Measurement of VOCs by event and location

| Event | Month | No days | Year | Total | Location | | | | | | | | |
|--------------|-----------|---------|------|-------|----------|------|---------------------------|-----|----------|-----|----------|-----|-----------|
| | | | | | GW | SSTE | Advanced Treatment Plants | | | | | | Sub-total |
| | | | | | | | Before MF | | After MF | | After RO | | |
| | | | | | | | KWRP | BPP | KWRP | BPP | KWRP | BPP | |
| 1 | November | 4 | 2006 | 370 | 0 | 0 | 159 | 0 | 53 | 0 | 158 | 0 | 370 |
| 2 | May/June | 6 | 2007 | 864 | 108 | 162 | 162 | 108 | 162 | 0 | 162 | 0 | 594 |
| 3 | September | 6 | 2007 | 778 | 0 | 0 | 168 | 168 | 53 | 53 | 168 | 168 | 778 |
| 4 | January | 6 | 2008 | 798 | 114 | 0 | 114 | 228 | 0 | 0 | 114 | 228 | 684 |
| 5 | April | 5 | 2008 | 784 | 0 | 56 | 112 | 224 | 0 | 56 | 112 | 224 | 728 |
| 6 | June | 5 | 2008 | 732 | 0 | 0 | 162 | 200 | 54 | 54 | 108 | 154 | 732 |
| Total | | 32 | | 4,326 | 222 | 218 | 877 | 928 | 322 | 163 | 822 | 774 | 3,886 |

GW: groundwater; SSTE: Subiaco secondary treated effluent; KWRP, Kwinana Water Reclamation Plant; BPP, Beenyup Pilot Plant; MF: microfiltration; RO: reverse osmosis

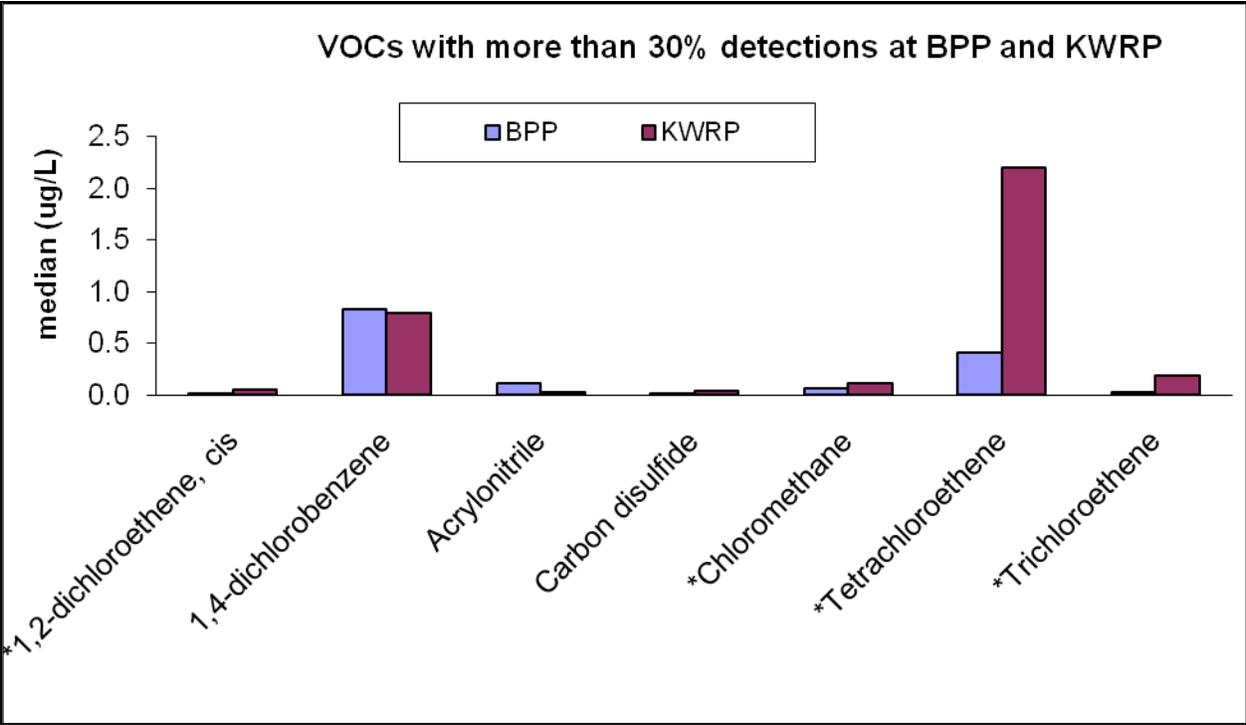


Figure 1: Median VOCs concentration in STE by plant in µg/L

*VOCs with statistically significant differences in concentrations between plants.

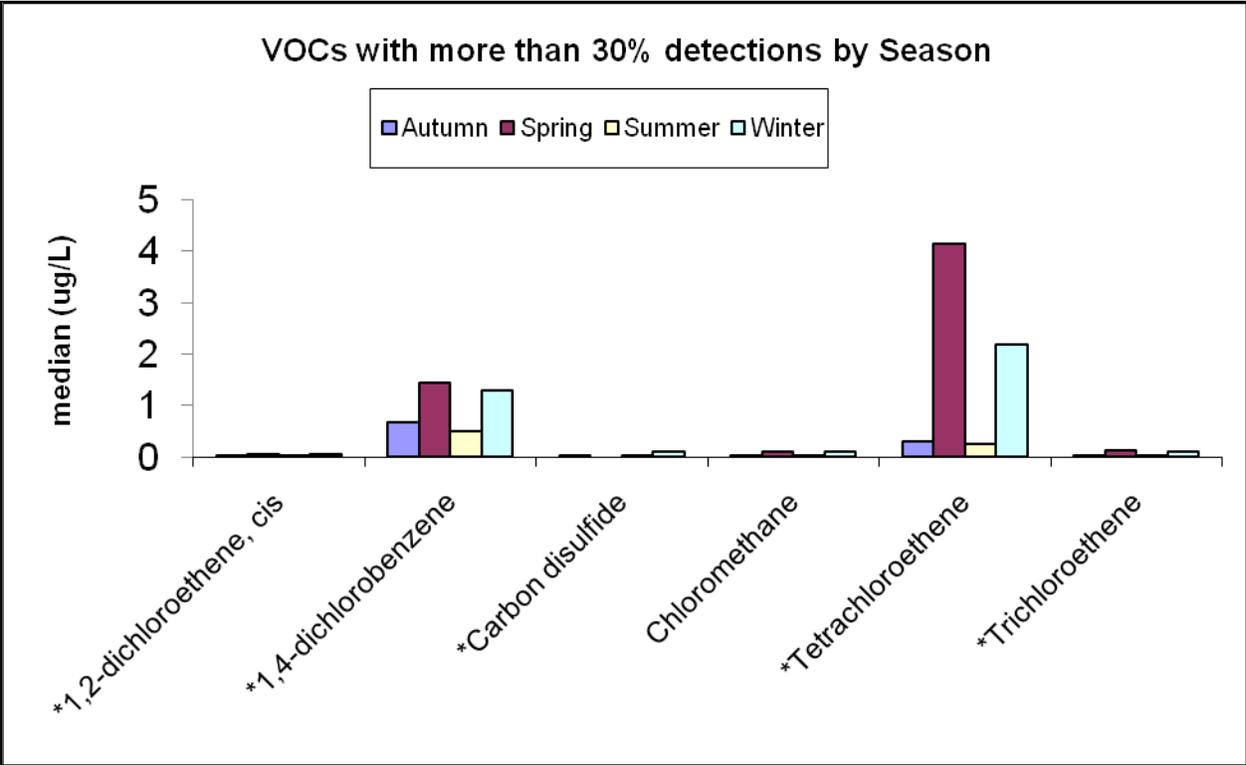


Figure 2: Median VOCs concentration in STE by season in µg/L

* VOCs with statistically significant differences among seasons. Acrylonitrile only analysed during spring

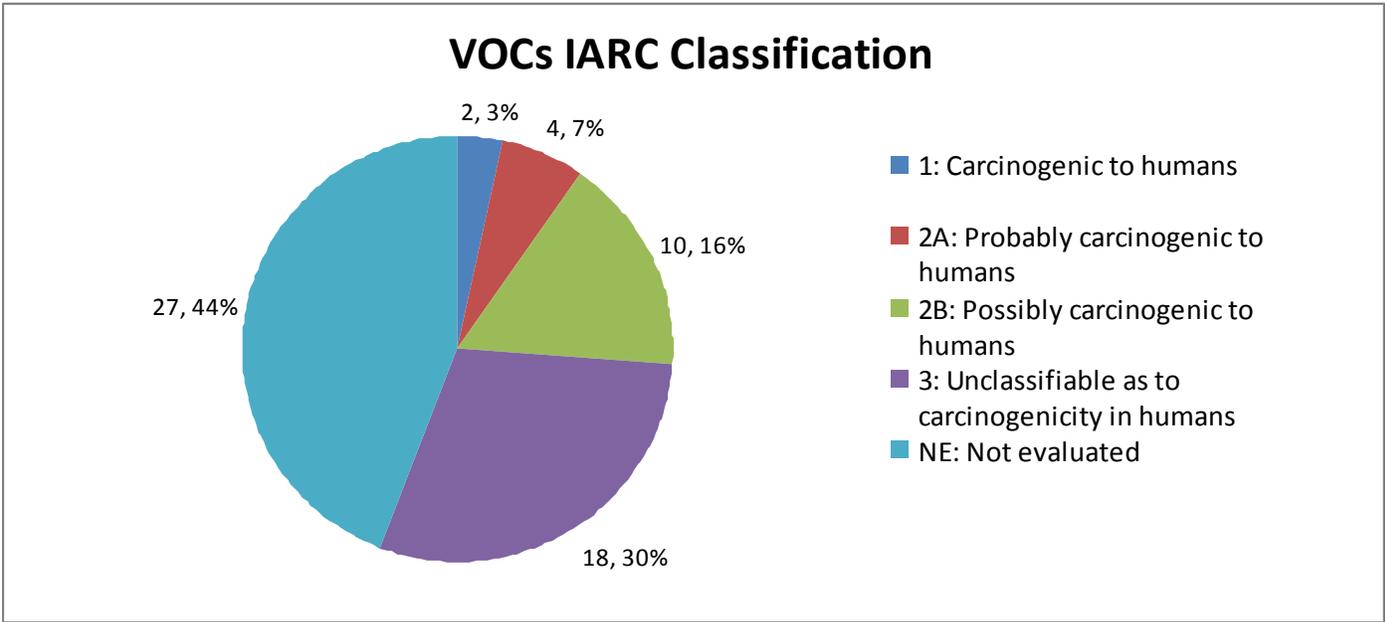


Figure 3: Distribution of the VOCs analysed according to the IARC Cancer Classification.

Table 2: VOCs detected in secondary treated effluent, post-MF and/or post-RO water

| | | | | | | | STE samples | | | | Post-MF samples | | | | Post-RO samples | | | |
|-------------------------|----------|-----------------------|-----------------------------|------|---------------------------|---------------|-------------|-------------------|----------------|-------------|-----------------|-------------------|----------------|-------------|-----------------|-------------------|----------------|-------------|
| Parameter | CASR No | Mean LOD (µg/L) | SRU (%) (0.5 µg/L) | Tier | Health value (µg/L) | Source | n | % of detection | RQ (median) | RQ (max) | n | % of detection | RQ (median) | RQ (max) | n | % of detection | RQ (median) | RQ (max) |
| 1,1,2-Trichloroethane | 79-00-5 | 0.099 | 31.2 | 1 | 5 | USEPA 2009 | 29 | 3.5 | 0.02 | 0.04 | | | | | | | | |
| 1,2,4-trimethylbenzene | 95-63-6 | 0.041 | 20.8 | 2 | 330 | CDPH 2010 | 28 | 3.6 | 0.0001 | 0.0002 | 9 | 66.7 | 0.0007 | 0.009 | 26 | 7.7 | 0.0001 | 0.0002 |
| 1,2-Dichloropropane | 78-87-5 | 0.018 | 16.4 | 1 | 40 | WHO 2006 | 29 | 10.3 | 0.0005 | 0.005 | 9 | 11.1 | 0.0005 | 0.004 | | | | |
| 1,2-dichlorobenzene | 95-50-1 | 0.026 | 17.7 | 1 | 40 | ADWG 2011 | 29 | 10.3 | 0.00003 | 0.0001 | 9 | 55.6 | 0.00003 | 0.003 | 27 | 3.7 | 0.000007 | 0.0002 |
| 1,2-dichloroethane | 107-06-2 | 0.017 | 8.4 | 1 | 3 | ADWG 2011 | 29 | 10.3 | 0.007 | 0.02 | | | | | 27 | 3.7 | 0.003 | 0.02 |
| 1,2-dichloroethene, cis | 156-59-2 | 0.030 | 13.2 | 1 | 60 | ADWG 2011 | 29 | 34.5 | 0.0009 | 0.002 | 9 | 55.6 | 0.002 | 0.003 | 27 | 3.7 | 0.0004 | 0.0009 |
| 1,3-dichlorobenzene | 541-73-1 | 0.056 | 20.9 | 2 | 600 | CDPH 2010 | 29 | 10.3 | 0.00003 | 0.001 | 9 | 11.1 | 0.0002 | 0.001 | 27 | 11.1 | 0.00003 | 0.0002 |
| 1,4-dichlorobenzene | 106-46-7 | 0.032 | 15.9 | 1 | 1500 | ADWG 2011 | 29 | 93.1 | 0.02 | 0.08 | 9 | 100.0 | 0.03 | 0.07 | 27 | 88.9 | 0.005 | 0.02 |
| Acrylonitrile | 107-13-1 | 0.030 | ND | 1 | 13 | CDPH 2010 | 6 | 50.0 | 0.003 | 0.01 | | | | | 6 | 83.3 | 0.01 | 0.02 |
| Benzene | 71-43-2 | 0.046 | 30.4 | 1 | 1 | ADWG 2011 | 29 | 27.6 | 0.08 | 0.1 | 9 | 22.2 | 0.08 | 0.08 | 27 | 29.6 | 0.08 | 0.1 |
| Bromomethane | 74-83-9 | 0.244 | 20.7 | 2 | 10 | USEPA 2009 | 29 | 3.5 | 0.002 | 0.02 | 9 | 11.1 | 0.02 | 0.02 | 27 | 7.4 | 0.002 | 0.02 |
| Carbon disulfide | 75-15-0 | 0.045 | 53.4 | 2 | 700 | IRIS | 15 | 80.0 | 0.00002 | 0.0006 | 3 | 100.0 | 0.0003 | 0.001 | 15 | 40.0 | 0.00002 | 0.0002 |
| Chloroethane | 75-00-3 | 0.033 | 23.2 | 3 | 0.7 | TTC | 29 | 24.1 | 0.04 | 0.8 | 9 | 33.3 | 0.09 | 0.8 | 27 | 11.1 | 0.03 | 0.09 |
| Chloromethane | 74-87-3 | 0.066 | 20.1 | 2 | 30 | USEPA 2009 | 29 | 62.1 | 0.004 | 0.02 | 9 | 88.9 | 0.006 | 0.03 | 27 | 63.0 | 0.003 | 0.01 |

| | | | | | | | | | | | | | | | | | | |
|-------------------------|------------|-------|------|---|------|------------|----|------|---------|--------|---|------|--------|--------|----|------|--------|--------|
| Dichlorodifluoromethane | 75-71-8 | 0.272 | 21 | 2 | 1000 | USEPA 2009 | 24 | 4.2 | 0.0002 | 0.0005 | 7 | 14.3 | 0.0005 | 0.0005 | 22 | 4.6 | 0.0002 | 0.0005 |
| Dichloromethane | 75-09-2 | 0.091 | 32.6 | 1 | 4 | ADWG 2011 | 8 | 12.5 | 0.02 | 0.05 | | | | | | | | |
| Ethylbenzene | 100-41-4 | 0.078 | 37 | 1 | 300 | ADWG 2011 | | | | | 9 | 66.7 | 0.0005 | 0.004 | 26 | 7.7 | 0.0002 | 0.0005 |
| MTBE | 1634-04-4 | 1.471 | 32 | 1 | 50 | WHO 2006 | 26 | 3.9 | 0.03 | 0.13 | | | | | 24 | 4.2 | 0.03 | 0.04 |
| Naphthalene | 91-20-3 | 0.031 | 41.7 | 2 | 100 | USEPA 2009 | | | | | 9 | 22.2 | 0.0002 | 0.02 | 27 | 7.4 | 0.0001 | 0.002 |
| Tetrachloroethene | 127-18-4 | 0.118 | 27.9 | 1 | 50 | ADWG 2011 | 29 | 86.2 | 0.009 | 0.2 | 9 | 88.9 | 0.05 | 0.2 | 27 | 14.8 | 0.003 | 0.006 |
| Toluene | 108-88-3 | 0.109 | 30.2 | 1 | 800 | ADWG 2011 | 28 | 14.3 | 0.0002 | 0.0003 | 9 | 88.9 | 0.0004 | 0.008 | 26 | 26.9 | 0.0002 | 0.002 |
| Trichloroethene | 79-01-6 | 0.029 | 17 | 1 | 20 | WHO 2006 | 29 | 48.3 | 0.003 | 0.04 | 9 | 55.6 | 0.02 | 0.03 | 27 | 7.4 | 0.001 | 0.003 |
| m-xylene | 108-38-3 | 0.087 | 48 | 1 | 600 | ADWG 2011 | | | | | 9 | 66.7 | 0.0003 | 0.004 | 26 | 7.7 | 0.0002 | 0.0003 |
| n-butylbenzene | 104-51-8 | 0.052 | 53.7 | 2 | 260 | CDPH 2010 | | | | | 9 | 22.2 | 0.0003 | 0.003 | 26 | 3.9 | 0.0002 | 0.0003 |
| o-xylene | 95-47-6 | 0.042 | 18.2 | 1 | 600 | ADWG 2011 | 28 | 17.9 | 0.00005 | 0.0001 | 9 | 88.9 | 0.0005 | 0.004 | 26 | 15.4 | 0.0001 | 0.0001 |
| p-xylene | 106-42-3 | 0.099 | 40.2 | 1 | 600 | ADWG 2011 | | | | | 9 | 66.7 | 0.0004 | 0.006 | 26 | 15.4 | 0.0002 | 0.0004 |
| 1,2,3-Trichlorobenzene | 87-61-6 | 0.027 | 52.6 | 1 | 30 | ADWG 2011 | | | | | | | | | 27 | 3.7 | 0.0005 | 0.004 |
| Chlorobenzene | 108-90-7 | 0.033 | 13.2 | 1 | 300 | ADWG 2011 | | | | | | | | | 27 | 11.1 | 0.0001 | 0.0002 |
| tert butylbenzene | 98-06-6 | 0.080 | 31.7 | 2 | 260 | CDPH 2010 | | | | | | | | | 27 | 3.7 | 0.0004 | 0.0005 |
| 1,3,5-trimethylbenzene | 108-67-8 | 0.083 | 59 | 2 | 330 | CDPH 2010 | | | | | 9 | 66.7 | 0.0004 | 0.002 | | | | |
| 1,3-Dichloropropene | 542-75-6 | 0.017 | 20.1 | 1 | 100 | ADWG 2011 | | | | | 9 | 11.1 | 0.0001 | 0.0003 | | | | |
| 2-propyltoluene | 28729-54-6 | 0.047 | 26.7 | 3 | 7 | TTC | | | | | 8 | 25 | 0.01 | 0.3 | | | | |

| | | | | | | | | | | | | | | | | | | |
|--------------------------------------|----------|-------|------|---|-----|--------------|--|--|--|--|---|------|-------|-------|--|--|--|--|
| Styrene | 100-42-5 | 0.136 | 37.4 | 1 | 30 | ADWG 2011 | | | | | 9 | 44.4 | 0.01 | 0.04 | | | | |
| Trichlorofluoromethane (Freon 11) | 75-69-4 | 0.096 | 50.4 | 1 | 150 | CDPH 2008 | | | | | 9 | 11.1 | 0.001 | 0.002 | | | | |
| p-Isopropyltoluene | 99-87-6 | 0.057 | 34.6 | 3 | 7 | TTC | | | | | 9 | 22.2 | 0.02 | 0.02 | | | | |

LOD: limit of detection; CASR No: registry number for each chemical assigned by the Chemical Abstracts Service, a division of the American Chemical Society; SRU: Standard Relative Uncertainty; n: total number of sample; STE: secondary treated effluent; all values are expressed in µg/L; RQ: risk quotient; CDPH: California Department of Public Health; IRIS: Integrated Risk Information System of the US EPA; TTC: Threshold of Toxicological Concern. ND: not determined

Table 3: VOCs without detections in any of the samples and corresponding “worst-case scenario” RQs

| Parameter | CASR No | Mean LOD (µg/L) | SRU (%) (0.5 µg/L) | n | Tier | Health value (µg/L) | Source | RQ |
|---|-----------|-----------------|--------------------|----|------|---------------------|------------|---------|
| 1,1,1,2-Tetrachloroethane | 630-20-6 | 0.076 | 27.8 | 73 | 2 | 1 | USEPA 2009 | 0.08 |
| 1,1,1-Trichloroethane | 71-55-6 | 0.037 | 14.3 | 73 | 1 | 200 | USEPA 2009 | 0.0002 |
| 1,1,2,2-Tetrachloroethane | 79-34-5 | 0.022 | 12.2 | 73 | 1 | 1 | CDPH 2008 | 0.02 |
| 1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113) | 76-13-1 | 0.029 | 28.2 | 24 | 1 | 1200 | CDPH 2008 | 0.00002 |
| 1,1-dichloroethane | 75-34-3 | 0.065 | 12.3 | 73 | 1 | 5 | CDPH 2008 | 0.01 |
| 1,1-dichloroethene | 75-35-4 | 0.056 | 20.5 | 73 | 1 | 30 | ADWG 2011 | 0.002 |
| 1,1-dichloropropene | 563-58-6 | 0.039 | 23.7 | 73 | 3 | 0.7 | TTC | 0.06 |
| 1,2,3-Trichloropropane | 96-18-4 | 0.057 | 21.7 | 73 | 2 | 100 | USEPA 2009 | 0.0006 |
| 1,2,4-Trichlorobenzene | 120-82-1 | 0.024 | 55.3 | 73 | 1 | 30 | ADWG 2011 | 0.0008 |
| 1,2-Dibromomethane | 8003-07-4 | 0.100 | ND | 7 | 3 | 0.7 | TTC | 0.1 |
| 1,2-dibromo-3-chloropropane | 96-12-8 | 0.048 | 31.3 | 73 | 1 | 1 | WHO 2006 | 0.05 |
| 1,2-dichloroethene, trans | 156-60-5 | 0.041 | 21.5 | 73 | 1 | 50 | WHO 2006 | 0.0008 |
| 1,2-dichloropropene | 563-54-2 | 0.032 | 19.1 | 66 | 3 | 0.7 | TTC | 0.05 |
| 1,3-Dichloropropane | 142-28-9 | 0.077 | 23.8 | 73 | 3 | 0.7 | TTC | 0.1 |
| 2,2-Dichloropropane | 594-207 | 0.225 | 31.9 | 73 | 3 | 0.7 | TCC | 0.3 |
| 2-Chlorotoluene (ortho) | 95-49-8 | 0.174 | 41.3 | 73 | 2 | 140 | CDPH 2010 | 0.001 |
| 4-Chlorotoluene (para) | 106-43-4 | 0.260 | 83.6 | 73 | 2 | 140 | CDPH 2010 | 0.002 |

| | | | | | | | | |
|---|----------|-------|------|----|---|-----|------------|--------|
| Acrolein | 107-02-8 | 0.300 | ND | 12 | 2 | 3.5 | TGA 2010 | 0.09 |
| Bromobenzene | 108-86-1 | 0.137 | 38.3 | 73 | 2 | 70 | USEPA 2009 | 0.002 |
| Carbon tetrachloride | 56-23-5 | 0.052 | 24.3 | 73 | 1 | 3 | ADWG 2011 | 0.02 |
| Ethylene Dibromide (1,2-Dibromoethane) | 106-93-4 | 0.059 | 19.1 | 66 | 1 | 0.4 | WHO 2006 | 0.15 |
| Hexachlorobutadiene | 87-68-3 | 0.188 | 46.1 | 73 | 1 | 0.7 | ADWG 2011 | 0.3 |
| Isopropylbenzene | 98-82-8 | 0.156 | 43.8 | 73 | 2 | 770 | CDPH 2010 | 0.0002 |
| Vinyl Chloride | 75-01-4 | 0.074 | 22.8 | 73 | 1 | 0.3 | ADWG 2011 | 0.3 |
| n-propylbenzene | 103-65-1 | 0.205 | 64.2 | 73 | 3 | 7 | TTC | 0.03 |
| sec-butylbenzene | 135-98-8 | 0.025 | ND | 7 | 2 | 260 | CDPH 2010 | 0.0001 |

LOD: limit of detection; CASR No: registry number for each chemical, assigned by the Chemical Abstracts Service, a division of the American Chemical Society; SRU: Standard Relative Uncertainty; n: total number of samples; STE: secondary treated effluent; all values are expressed in µg/L; RQ: risk quotient; CDPH: California Department of Public Health; TTC: Threshold of Toxicological Concern; TGA: Therapeutic Goods Administration; ND: not determined

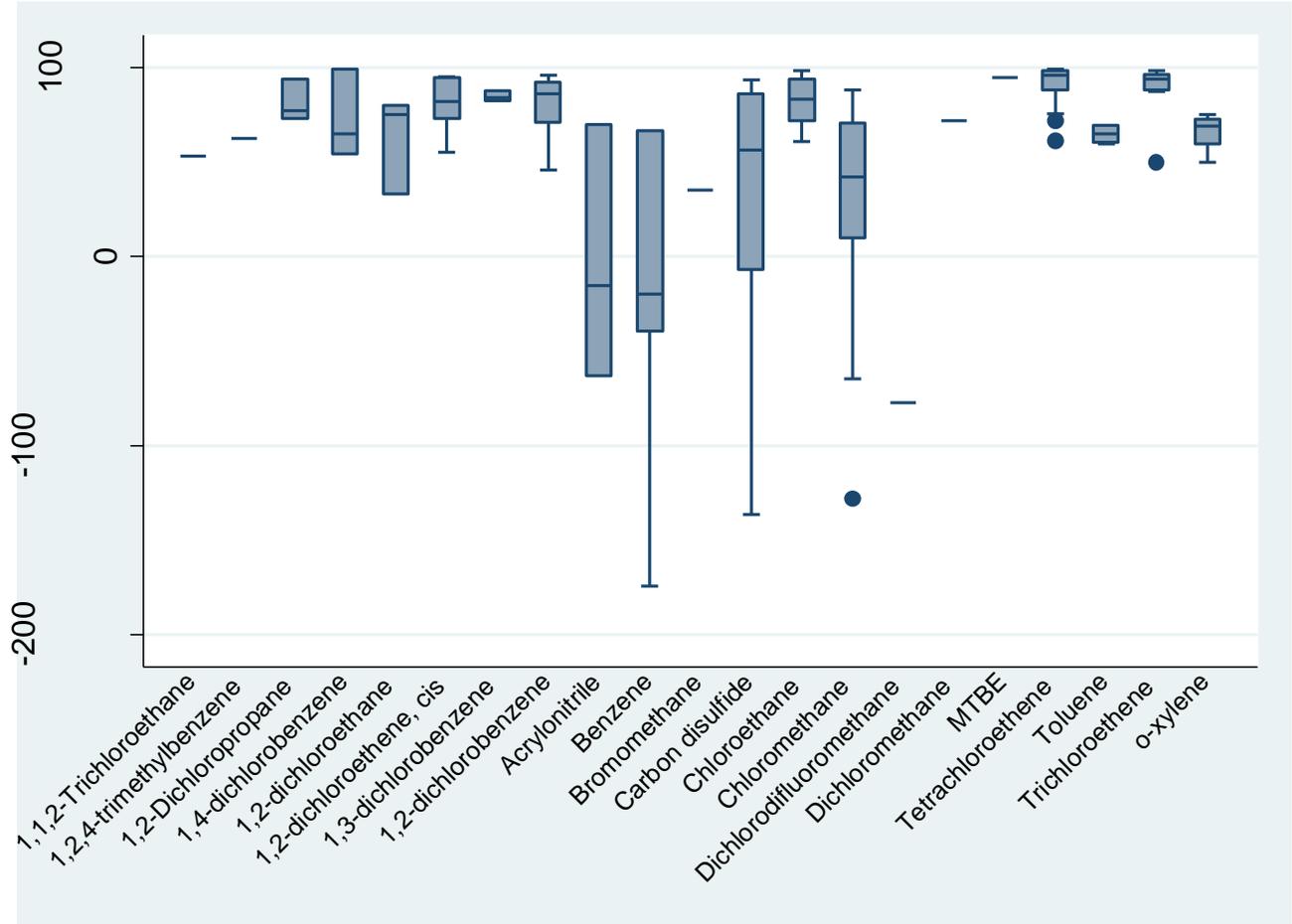


Figure 4: MF/RO removal efficiency of VOCs detected in secondary treated effluent. Bars indicate the median, 25th, 75th percentile and statistically determined minimum and maximum values; dots represent extreme values.

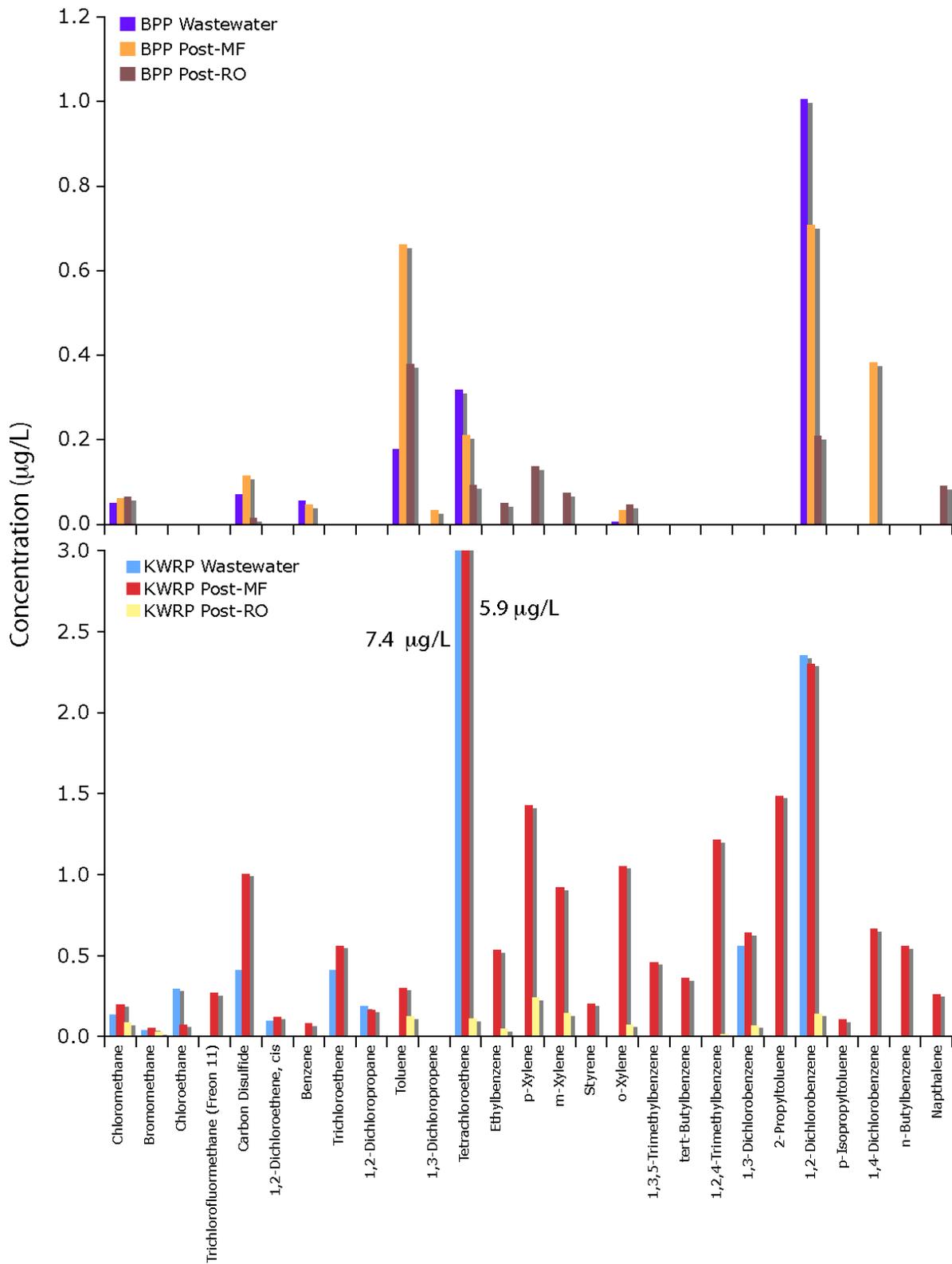


Figure 5: Median concentrations of VOCs in paired secondary treated effluent, post-MF

water and post-RO water samples for KWRP and BPP

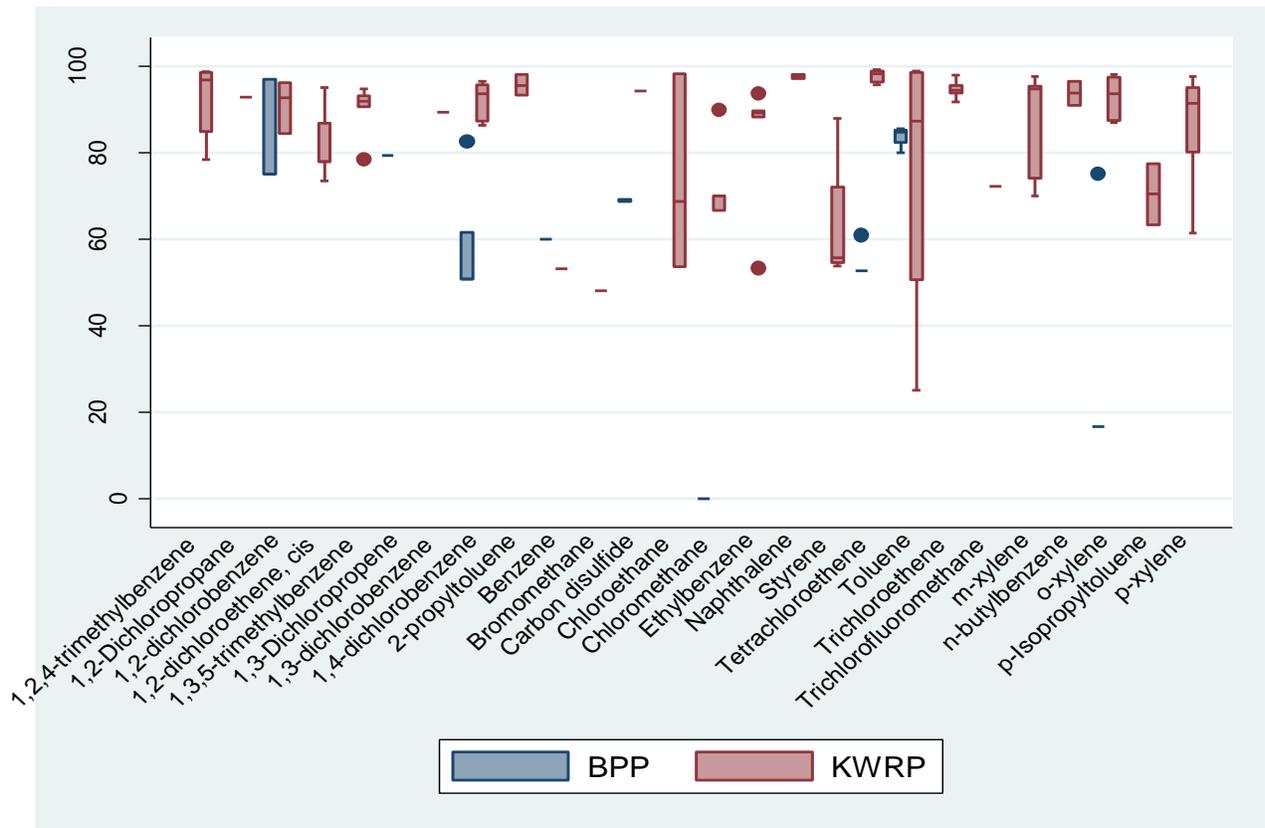


Figure 6: RO removal efficiency of VOCs detected in post-MF wastewater by plant. Bars indicate the median, 25th, 75th percentile and statistically determined minimum and maximum values; dots represent extreme values.