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ROZPRAWA DOKTORSKA

Tytuł rozprawy w języku polskim: **Zastosowanie technik instrumentalnych i sensorycznych do oceny jakości powietrza atmosferycznego z uwzględnieniem negatywnego oddziaływania na środowisko związków uciążliwych zapachowo powstałych z osadów ściekowych**

Tytuł rozprawy w języku angielskim: **The use of instrumental and sensory techniques to assess the quality of atmospheric air including the negative impact on the environment of odor compounds emitted from sewage sludge**

Promotor	Promotor pomocniczy
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Z tego miejsca pragnę bardzo serdecznie podziękować mojemu promotorowi
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za obecność w tych najtrudniejszych momentach.

Spis treści

Wykaz skrótów i akronimów

Skrót/Akronim	Termin anglojęzyczny	Termin polskojęzyczny
c	*Concentration of analyte*	Stężenie analitu
c_{od}	*Odor concentration*	Stężenie zapachowe
CR	*Carcinogenic Risk*	Ryzyko rakotwórcze
$(D/T)_{NIE}$	*Dilution-to-Threshold value at which the odor is not yet perceptible*	Stopień rozcieńczenia odpowiadający momentowi, w którym zapach nie był wyczuwalny jednakże bezpośrednio poprzedzał rozcieńczenie $(D/T)_{TAK}$
D/T)$_{TAK}$	*Dilution-to-Threshold value at which the odor is perceptible*	Stopień rozcieńczenia odpowiadający momentowi, w którym zapach był po raz pierwszy wyczuwalny
GCxGC-MS	*Two dimensional Gas Chromatography coupled with Mass Spectrometry*	Dwuwymiarowa chromatografia gazowa sprzężona ze spektrometrią mas
GCxGC-TOF-MS	*Two dimensional Gas Chromatography coupled with Time-of-Flight Mass Spectrometry*	Dwuwymiarowa chromatografia gazowa sprzężona ze spektrometrią mas i analizatorem czasu przelotu jonów fragmentacyjnych
GC-MS	*Gas Chromatography coupled with Mass Spectrometry*	Chromatografia gazowa sprzężona ze spektrometrią mas
GC-MS/MS	*Gas Chromatography coupled with Tandem Mass Spectrometry*	Chromatografia gazowa sprzężona z tandemową spektrometrią mas
GSS	*Gas Sampling System*	Urządzenie do pobierania próbek gazowych
HI	*Hazard Index*	Wskaźnik zagrożenia
LOD	*Limit of Detection*	Granica wykrywalności
QAV	*Odor Activity Value*	Współczynnik aktywności zapachowej
OT	*Odor Threshold*	Próg wyczuwalności zapachowej
PA	*Proton Affinity*	Powinowactwo do protonu
PTR-MS	*Proton Transfer Reaction – Mass Spectrometry*	Spektrometria mas z jonizacją poprzez reakcję przeniesienia protonu
PTR-IT-MS	*Proton Transfer Reaction – Ion Trap – Mass Spectrometry*	Spektrometria z jonizacją poprzez reakcję przeniesienia protonu sprzężona z analizatorem typu pułapka jonowa

PTR-GC-MS	*Proton Transfer Reaction – Gas Chromatography – Mass Spectrometry*	Spektrometria mas z jonizacją poprzez reakcję przeniesienia protonu sprzężona z chromatografią gazową
PTR-SRI-MS	*Proton Transfer Reaction – Selective Reagent Ionization – Mass Spectrometry*	Spektrometria mas z jonizacją poprzez reakcję przeniesienia protonu z możliwością wyboru selektywnego czynnika jonizującego
PTR-TOF-MS	*Proton Transfer Reaction Time-of-Flight Mass Spectrometry*	Spektrometria mas z jonizacją poprzez reakcję przeniesienia protonu sprzężona z analizatorem czasu przelotu jonów fragmentacyjnych
Q	*Quadrupole*	Analizator kwadrupolowy
Q-TOF	*Quadrupole Time-of-Flight*	Kwadrupolowy analizator czasu przelotu
QqQ	*Triple Quadrupole*	Analizator typu potrójny kwadrupol
PDMS	*Polydimethylsiloxane*	Poli(dimetylosikoksan)
SBSE	*Stir Bar Sorptive Extraction*	Ekstrakcja analitów za pomocą wirującego elementu sorpcyjnego
SPME	*Solid-Phase Microextraction*	Mikroekstrakcja do fazy stacjonarnej
TD	*Thermal Desorption*	Desorpcja termiczna
Z_{ITE}	*Individual odor detection threshold*	Ocena progu indywidualnego
Z_{NIE}	*Dilution corresponding to the D/T value at which the odor is not yet perceptible*	Stopień rozcieńczenia przy którym zapach nie był wyczuwalny
Z_{TAK}	*Dilution corresponding to the D/T value at which the odor is first perceived*	Stopień rozcieńczenia przy którym zapach był wyczuwalny

Streszczenie w języku polskim

Jakość powietrza atmosferycznego uwarunkowana jest w dużej mierze występowaniem związków chemicznych, wykazujących negatywne oddziaływanie na człowieka i środowisko, w którym on funkcjonuje. Ilość substancji chemicznych uwalnianych z obiektów przemysłowych i gospodarczych jest na tyle duża, iż prowadzenie badań związanych z ich scharakteryzowaniem stanowi poważne wyzwanie analityczne. Jedną z cech zanieczyszczeń powietrza atmosferycznego, w sposób istotny wpływającą na postrzeganie tych związków jest ich profil zapachowy. Obecność odorantów, zwłaszcza na terenach zlokalizowanych w bezpośrednim sąsiedztwie zabudowań, jest powodem skarg ludności na jakość powietrza atmosferycznego. Jednymi z obiektów gospodarki komunalnej, których funkcjonowanie w znaczący sposób przyczynia się do powstawania związków chemicznych wykazujących właściwości zapachowe, są oczyszczalnie ścieków. Są to z reguły zakłady zlokalizowane w sąsiedztwie silnie rozbudowanych aglomeracji miejskich.

W ramach realizowanej w trakcie studiów doktoranckich tematyki badawczej, podjęto próbę scharakteryzowania związków zapachowych uwalnianych z osadów ściekowych, będących jednym z odpadów stałych, powstających w coraz większych ilościach w oczyszczalniach ścieków. W tym celu wykorzystano zaawansowane rozwiązania aparaturowe wykorzystujące spektrometrię mas – technikę dwuwymiarowej chromatografii gazowej sprzężonej ze spektrometrią mas (GCxGC-MS), technikę chromatografii gazowej sprzężonej z tandemową spektrometrią mas (GC-MS/MS) oraz technikę spektrometrii mas z jonizacją poprzez reakcję przeniesienia protonu. Uzupełnieniem badań w oparciu o wykorzystanie technik instrumentalnych były analizy sensoryczne, przeprowadzone z zastosowaniem techniki olfaktometrii terenowej.

Na podstawie przeprowadzonych badań możliwe było określenie zapachowego potencjału osadów ściekowych, poprzez oznaczenie zawartości substancji zapachowych o największych stężeniach, mogących pełnić rolę markerów uciążliwości zapachowej, związanej z przetwarzaniem osadów ściekowych. Wykazano także, iż obecność tych

związków może wpływać na pogorszenie stanu zdrowia pracowników oczyszczalni i mieszkańców pobliskich terenów. Wykazano również, że przefermentowane osady ściekowe poddane procesom odwadniania mogą nadal stanowić źródło emisji wielu szkodliwych związków zapachowych, powstających w trakcie procesów ich starzenia. Informacja ta jest istotna ze względu na konieczność stosowania dodatkowych operacji i procesów, mających na celu zmniejszenie negatywnego oddziaływania na środowisko osadów ściekowych przeznaczonych do zagospodarowania, np. w budownictwie lub rolnictwie. Wykazano również, iż możliwe jest wykorzystanie informacji dotyczących poziomu emisji związków zapachowych na poszczególnych etapach przetwarzania osadów ściekowych, w celu opracowywania nowych rozwiązań metodycznych w zakresie minimalizacji ich negatywnego oddziaływania na środowisko.

Streszczenie z języku angielskim

The quality of atmospheric air is strongly conditioned by the presence of chemical compounds, which cause negative impact on human and the environment. The amount of chemical compounds emitted from industrial and municipal plants is large enough, that conducting of research including their characteristics is a major analytical challenge. One of the most important features of air pollution, which can have a significant impact on their perception, is odor profile. The presence of odorants, especially in the areas located in the immediate vicinity of residential buildings is the reason of complaints of the population about the quality of atmospheric air. One of the main objects of the municipal economy, that functioning significantly contributes to the generation of chemical compounds exhibiting aroma properties, are wastewater treatment plants. These are usually plants located in a strongly developed urban agglomerations.

As a part of the research topics conducted during my PhD studies, an attempt was made to characterize volatile aromatic compounds emitted from sewage sludge, which is the one of the main solid waste generated in increasing quantities in wastewater treatment plants. For this purpose, a two-dimensional gas chromatography coupled with mass spectrometry (GCxGC-MS), gas chromatography coupled with tandem mass spectrometry (GC-MS/MS) and proton transfer reaction – mass spectrometry (PTR-MS) were applied. As a supplementation of instrumental research, sensory analysis was carried out using field olfactometry technique.

On the basis of the conducted research, it was possible to estimate the odor potential of sewage sludge by determination of odor compounds that could be potential markers of odor nuisance associated with the processing of sewage sludge. It was also shown that the presence of these compounds may affect the health condition of workers in the wastewater treatment plant and residents of nearby areas. The conducted research allowed to demonstrate that dewatered digested sludge may still be a source of emission of many harmful volatile aromatic compounds, generated during the aging of sludge. This information is important due to the necessity to use additional operations

and processes aimed at reducing the negative environmental impact of sewage sludge to be used, e.g. in construction or agriculture. The results obtained during PhD studies demonstrated, that it is possible to use information concerning the emission level of volatile aromatic compounds at particular stages of sewage sludge treatment, in order to develop new methodological solutions in the area of minimizing their negative impact on the environment.

I CZĘŚĆ LITERATUROWA

1. Wprowadzenie

Intensywny rozwój gospodarczy i przemysłowy, obserwowany w wielu krajach na całym świecie, wiąże się nierozerwalnie z ryzykiem wprowadzania do środowiska ogromnych ilości substancji chemicznych, mogących negatywnie oddziaływać na środowisko. Jedną ze składowych środowiska, szczególnie narażoną na ich występowanie jest powietrze atmosferyczne [1]. Stanowi ono układ niezwykle złożony, ulegający zmianom nawet w bardzo krótkich odstępach czasu. Dlatego też badania dotyczące składu chemicznego powietrza nie należą do zadań łatwych, niemniej jednak niezwykle istotnych dla środowiska nieożywionego i ożywionego, w tym dla ludzi [2].

Obecność w powietrzu atmosferycznym substancji chemicznych może w istotny sposób wpływać zarówno na stan zdrowia człowieka jak i na poziom komfortu jego życia. Jedną z grup zanieczyszczeń szczególnie mocno oddziałujących na środowisko a zwłaszcza na ludzi są odory [3]. Terminem tym określane są lotne związki chemiczne pobudzające receptory węchowe, w wyniku czego jesteśmy w stanie stwierdzić ich obecność [4]. Substancje te występują w powietrzu atmosferycznym niemal zawsze jako mieszaniny związków o zróżnicowanych właściwościach zapachowych, takich jak rodzaj zapachu, intensywność zapachowa, jakość hedoniczna czy też próg wyczuwalności zapachowej poszczególnych substancji [5,6].

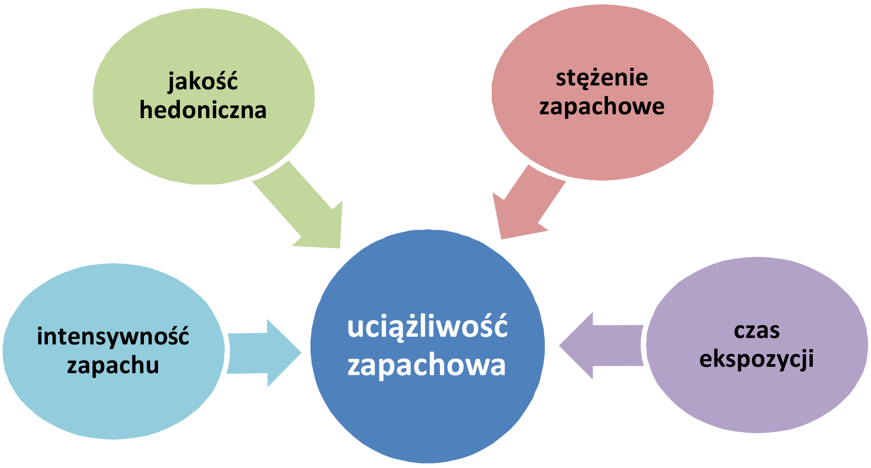
Obecność związków zapachowych w powietrzu atmosferycznym może powodować szereg niepożądanych reakcji organizmu, takich jak niepokój, stres, bóle i zawroty głowy, problemy z koncentracją, mdłości, zmniejszenie apetytu, napięcie emocjonalne oraz kłopoty z zasypianiem. Negatywny wpływ odorów może obejmować również dyskomfort związany z długotrwałym odczuwaniem nieprzyjemnego zapachu [7]. Negatywne oddziaływanie związków zapachowych dotyczy w szczególności mieszkańców terenów bezpośrednio sąsiadujących z obiektami komunalnymi i przemysłowymi stanowiącymi źródło ich emisji. Postępujący w ostatnich latach rozwój urbanizacji sprawia, iż obiekty te znajdują się w coraz bliższym sąsiedztwie zabudowań mieszkalnych, w wyniku czego skala problemu w najbliższym czasie może ulec znacznemu powiększeniu. Dyskomfort związany z obecnością substancji zapachowych oraz okolicznościom związanym z ich występowaniem, określany jako uciążliwość zapachowa, jest wynikiem oddziaływań wielu czynników, mogących wzajemnie wzmacniać lub osłabiać reakcje danej osoby na bodźce zapachowe [8]. Odczucia związane z obecnością substancji zapachowych to zarówno indywidualne uwarunkowania organizmu jak i szereg czynników zewnętrznych, takich jak stopień zmęczenia organizmu spowodowany wysiłkiem fizycznym lub umysłowym, obecność w środowisku innych zanieczyszczeń mogących oddziaływać na organizm człowieka czy też inne czynniki takie jak hałas, wilgotność oraz poziom zapylenia powietrza [9].

Powstawanie związków zapachowych wiąże się z funkcjonowaniem obiektów komunalnych i przemysłowych, w tym m. in. oczyszczalni ścieków [10]. Uciążliwość zapachowa w tego typu obiektach jest związana głównie z działalnością mikroorganizmów, obecnych zarówno w ściekach jak i osadach ściekowych. W wyniku licznych przemian – głównie o charakterze beztlenowym – może występować zwiększona emisja związków zapachowych [11]. Nieodłącznym elementem procesu oczyszczania dostarczanych ścieków są powstające w osadnikach wstępnych oraz wtórnych osady ściekowe. Ich przetwarzanie wiąże się z licznymi operacjami i procesami jednostkowymi. Zróżnicowany skład fizyko-chemiczny osadów ściekowych znacząco utrudnia opracowanie skutecznych metod redukcji negatywnego wpływu na środowisko związków zapachowych w nich zawartych [12]. Zagadnienia te nie zostały do tej pory w sposób wyczerpujący opisane w literaturze naukowej.

2. Odory jako zanieczyszczenia powietrza atmosferycznego

2.1. Charakterystyka związków zapachowych obecnych w powietrzu atmosferycznym

Określenie poziomu oddziaływania związków zapachowych na organizm człowieka jest trudne do osiągnięcia ze względu na fakt, iż postrzeganie zapachu ma charakter indywidualny. W trakcie prowadzenia badań ukierunkowanych na ocenę ryzyka występowania zjawiska uciążliwości zapachowej, uwzględniane są cztery podstawowe cechy zapachu przedstawione na rysunku 1: stężenie zapachowe, intensywność zapachowa, jakość hedoniczna oraz czas ekspozycji.



Rysunek 1. Najważniejsze składowe zjawiska uciążliwości zapachowej.

Zgodnie z normą PN-EN 13725:2007 „Jakość powietrza. Oznaczanie stężenia zapachowego metoda olfaktometrii dynamicznej", stężenie zapachowe definiowane jest jako liczba europejskich jednostek zapachowych w metrze sześciennym w warunkach standardowych. Jednostkę zapachową zdefiniowano, odnosząc się do substancji wzorcowej - roztworu n-butanolu. Osiągnięcie 1 ou_E/m^3 stwierdzamy wtedy, gdy zapach jest tak samo silny, jak zapach 123 µg n-butanolu odparowanego do 1 m^3 gazu obojętnego. Z pojęciem stężenia zapachowego nierozerwalnie wiąże się pojęcie indywidualnego progu wyczuwalności zapachowej. Za próg wyczuwalności węchowej uznaje się takie stężenie danej substancji zapachowej, które wywołuje wrażenie węchowe u 50% osób poddanych jej oddziaływaniu [13]. W praktyce pomiarowej za próg wyczuwalności uznaje się wymagane rozcieńczenie badanej próbki gazowej zawierającej związki zapachowe, aby prawdopodobieństwo rozpoznania jej zapachu wynosiło 50% [14]. Wyrażanie stężenia zapachowego zgodnie z normą PN-EN 13725:2007, umożliwia obliczenie strumienia emisji zapachu, poprzez przemnożenie stężenia zapachowego (wyrażanego w $ou_{E/}m^3$) przez objętościowe natężenie przepływu strumienia gazów zawierających związki zapachowe (wyrażanego z m^3/s). Uzyskuje się wówczas wielkość emisji wyrażoną w ou_E/s [15]. Wprowadzenie definicji stężenia zapachowego oraz progu wyczuwalności zapachowej było związane z wprowadzeniem w Polsce jednolitej dla wszystkich państw Unii Europejskiej metodyki pomiaru związków zapachowych, opisanej we wspomnianej normie. W przypadku wyznaczania stężenia zapachowego zgodnie z metodyką opisaną we wspomnianej normie, przyjmuje się oznaczenie jednostki zapachowej symbolem ou_E. W przypadku stosowania innej metodyki stężenie zapachowe wyraża się za pomocą jednostki zapachowej ou, bez umieszczania litery „E" w indeksie dolnym [16,17].

Intensywność zapachowa definiowana jest jako „siła odczuwanego zapachu" i jest bezpośrednio związana z mocą wrażeń węchowych kojarzonych intuicyjnie [18]. W celu wyznaczenia tego parametru najczęściej stosuje się skale punktowe, werbalne oraz wzorcowe. Jednym z przykładów skali punktowej jest 6-stopniowa skala opisana w niemieckich wytycznych VDI 3940. Na jej podstawie osoby oceniające zapach mają za zadanie przypisać intensywności zapachowej odpowiednią wartość liczbową.

Tabela 1 Skala intensywności zapachowej zgodnie z normą VDI 3940.

opis siły zapachu	**stopień intensywności**
zapach skrajnie mocny	6
zapach bardzo mocny	5
zapach mocny	4
zapach wyraźny	3
zapach słaby	2
zapach bardzo słaby	1
brak zapachu	0

Oddziaływanie hedoniczne, określane również jako jakość hedoniczna definiowane jest jako oddziaływanie danej substancji chemicznej, w wyniku którego następuje przypisanie występującego wrażenia węchowego a następnie jego ocena między skrajnymi określeniami – skrajnie przyjemny – skrajnie nieprzyjemny [19,20]. W przypadku jakości hedonicznej – podobnie jak w przypadku intensywności zapachowej – wyznaczenie tego parametru odbywa się najczęściej z zastosowaniem skali werbalnych, graficznych lub punktowych.

Tabela 2 Skala jakości hedonicznej zgodnie z normą VDI 3940.

-4	-3	-2	-1	0	+1	+2	+3	+4
zapach skrajnie nieprzyjemny				brak zapachu			zapach skrajnie przyjemny	

2.2. Metody wykrywania i oznaczeń związków zapachowych

Określenie poziomu emisji związków zapachowych powstających podczas poszczególnych operacji i procesów jednostkowych, przeprowadzanych w oczyszczalniach ścieków wiąże się z koniecznością doboru odpowiednich technik pomiarowych, uwzględniających m.in. przewidywany poziom stężeń oznaczanych związków, czy też ryzyko utraty części analitów wskutek nieprawidłowego postępowania w trakcie pobierania i transportu próbek [11]. Biorąc pod uwagę najogólniejszą klasyfikację technik powszechnie stosowanych do oceny oddziaływania zapachowego wynikającego z funkcjonowania oczyszczalni ścieków, należy wyróżnić dwie główne grupy technik – techniki instrumentalne oraz techniki sensoryczne [21].

2.2.1 Techniki instrumentalne

Zastosowanie wybranych technik instrumentalnych umożliwia przeprowadzenie analizy jakościowej oraz ilościowej badanych próbek pod kątem związków zapachowych [22]. Uzyskane informacje o składzie chemicznym próbek powietrza atmosferycznego dają możliwość wstępnego oszacowania poziomu emisji gazowych zanieczyszczeń powietrza atmosferycznego na założonym obszarze [23].

Jedną z najczęściej stosowanych technik instrumentalnych stosowanych do przeprowadzenia oznaczeń związków zapachowych jest technika chromatografii gazowej sprzężona ze spektrometrią mas (GC-MS*)* [24]. Rozwiązanie to umożliwia oznaczanie analitów występujących na bardzo niskim poziomie stężeń (w zależności od budowy spektrometru mas są to stężenia rzędu ng/ml – pg/ml). W przypadku analizy próbek o złożonym składzie matrycy dobrym rozwiązaniem wydaje się technika dwuwymiarowej chromatografii gazowej sprzężonej ze spektrometrią mas (GCxGC-MS) [25]. W przypadku tej techniki anality rozdzielane w pierwszej kolumnie chromatograficznej opuszczając ją kierowane są do modulatora, stanowiącego centralny element układu GCxGC-MS. Następnie wprowadzane są do drugiej kolumny chromatograficznej charakteryzującej się typem fazy stacjonarnej o odmiennej polarności względem fazy stacjonarnej stanowiącej wypełnienie pierwszej kolumny [26,27]. W układach GCxGC-MS najczęściej stosowany jest układ, w którym pierwsza z kolumn wypełniona jest niepolarną fazą stacjonarną, natomiast wypełnienie drugiej kolumny stanowi faza stacjonarna średniopolarna. Dostępne są również inne kombinacje układu kolumn chromatograficznych, w zależności od rodzaju analitów oraz składu matrycy [28].

Modyfikacje w zakresie techniki GC-MS mogą dotyczyć również budowy spektrometru mas. Jednym z takich przykładów jest technika chromatrografii gazowej sprzężonej z tandemową spektrometrią mas (GC-MS/MS). W przypadku tej techniki jony powstające w źródle jonów przemieszczają się przez układ dwóch połączonych ze sobą analizatorów [29]. Najczęściej stosowanymi rozwiązaniami są zestaw dwóch analizatorów kwadrupolowych połączonych ze sobą celą kolizyjną (QqQ) albo układ połączonych ze sobą analizatorów kwadrupolowy + analizator czasu przelotu jonów fragmentacyjnych (Q-TOF) [30]. Tandemowy spektrometr mas jako detektor w połączeniu z układem chromatograficznych daje znacznie większe możliwości zarówno pod względem czułości jak i rozdzielczości w porównaniu ze spektrometrem mas wyposażonym w pojedynczy analizator [31]. W tabeli 3 przedstawiono wybrane przykłady stosowania technik instrumentalnych do oznaczania związków zapachowych obecnych w powietrzu atmosferycznym.

Tabela 3 Przykłady zastosowania technik instrumentalnych w celu oznaczania związków zapachowych obecnych w powietrzu atmosferycznym.

technika	pobieranie analitów	typ sorbentu	faza ruchoma	kolumna chromatograficzna	analizator	LOD	lit.
GC-MS	TD	Tenax TA	Hel (1,0 ml/min)	HP5-MS (30 m x 0,25 mm x 0,25 μm)	Q	0,005-15,23 ng	[32]
GC-MS	SPME	Carboxen - PDMS	Hel (1,0 ml/min)	HP-5MS (30 m x 0,25 mm x 0,25 μm)	Q	-	[33]
GC-MS	TD	Tenax TA +Carbograph 5TD	Hel	HP-INNOWax (30 m x 0,25 mm x 0,25 μm)	Q	0,001-0,1 nL/L	[34]
GC-MS	TD	Tenax TA	Hel (1,8 ml/min)	DB-VRX	Q	0,22-1,48 $\mu g/m^3$	[35]
GCxGC-MS	TD	Tenax TA	Hel (1,0 ml/min)	Equity 1 (30 m x 0,25 mm x 0,25 μm); Sol Gel Wax (2,0 m x 0,10 mm x 0,10 μm)	TOF	-	[36]
GCxGC-MS	TD	Carbograph 5TD + Carbograph 2TD	Hel (1,5 ml/min)	HP5MS (30 m x 0,25 mm x 1,0 μm); HP INNOWax (2,5 m x 0,18 mm x 0,18 μm)	Q	-	[37]
GCxGC-MS	TD	Carbopack B, Carbopack C, Carbosieve SIII	Hel	HP5 (30 m x 0,32 mm x 0,25 μm); BP 50*	TOF	-	[38]
GC-MS/MS	TD	Tenax TA	Hel	CD 624 (60 m x 0,25 mm x 1,44 μm)	QqQ	-	[39]
GC-MS/MS	SBSE	PDMS	Hel	DB5-MS (30 m x 0,25 mm x 0,25 μm)	QqQ	0,020-0,054 ng	[40]

* w pracy autorzy nie zamieścili wymiarów drugiej kolumny chromatograficznej

Wykorzystanie technik chromatograficznych w celu oznaczania substancji zapachowych obecnych w powietrzu atmosferycznym wiąże się niemal zawsze z koniecznością wcześniejszego przygotowania próbek do analizy [41]. Etap ten jest z reguły zarówno czasochłonny jak i pracochłonny. W wielu przypadkach towarzyszy temu znaczne zużycie rozpuszczalników organicznych, które powoduje, że zastosowana procedura analityczna jest niekorzystna z punktu widzenia wprowadzania do praktyki laboratoryjnej zasad zielonej chemii [42]. Na etapie przygotowania próbek istnieje ryzyko utraty części analitów co może powodować różnice między wynikami uzyskanymi w trakcie prowadzonych pomiarów a wartościami rzeczywistymi [43]. Kolejnym czynnikiem stanowiącym potencjalne ograniczenie w zakresie wykorzystania rozwiązań instrumentalnych jest czasochłonność analizy końcowej [30]. Ze względu na wymienione powyżej problemy trwają intensywne poszukiwania nowych rozwiązań metodycznych i aparaturowych, umożliwiających przeprowadzenie analizy w sposób szybki, bez konieczności przygotowania próbki do analizy.

Pośród wielu nowych dostępnych rozwiązań na szczególną uwagę zasługują techniki pomiarowe wykorzystujące spektrometrię mas. Jedną z takich technik jest technika spektrometrii mas wykorzystująca reakcję przeniesienia protonu (PTR-MS). Technika ta bazuje na przekształcaniu w postać zjonizowaną obojętnych cząsteczek w wyniku reakcji pomiędzy nimi a jonami hydroniowymi H_3O^+ [44]. W wyniku tej reakcji obojętne cząsteczki przyjmują jon H^+, przez co mogą być oznaczane w spektrometrze mas. Technika PTR-MS, jako jedna z technik zaliczana do bezpośrednich technik pomiarowych umożliwiających pomiar w czasie rzeczywistym, bazuje na jonizacji chemicznej. Jony hydroniowe H_3O^+, wytwarzane są w źródle jonów z cząsteczek pary wodnej, w wyniku procesów elektrodowych zachodzących na katodzie wnękowej. Reakcja wymiany protonu zachodzi w kolejnej części urządzenia – komorze dryfu, w atmosferze gazu obojętnego [45]. Technika PTR-MS bardzo dobrze sprawdza się w przypadku oznaczania związków organicznych występujących w powietrzu atmosferycznym, w tym również związków uciążliwych zapachowo, zarówno pochodzenia naturalnego jak i antropogenicznego [46]. Znacząca większość tych związków odznacza się mniejszą wartością parametru określającego powinowactwo do protonu (PA), którego to wartość powinna być wyższa od wartości PA dla wody, wynoszącej 691,53 kJ/mol [47]. W przypadku nielicznych związków z grupy LZO, dla których wartość tego parametru jest niższa od PA wody, możliwe jest zastosowanie trybu pracy spektrometru z innym źródłem jonów reakcyjnych, np. Kr^+, NO^+, Xe^+ czy też O_2^+ (PTR-SRI-MS). Rozwiązanie to jest również przydatne w przypadku konieczności rozdzielania związków izobarycznych, których rozdzielanie z zastosowaniem jonów hydroniowych jako jonów reakcyjnych jest trudne do osiągnięcia [48, 49]. Jednym z takich przypadków jest rozdzielanie mieszaniny zawierającej keton metylowo-winylowy oraz metakrolinę, związki stanowiące produkty oksydacji izoprenu, które w wyniku przyłączenia jonu H^+ tworzą jony o identycznej masie cząsteczkowej. W przypadku przeprowadzenia reakcji obydwu wyżej wymienionych związków z jonem NO^+, produktami końcowymi są jony o różnej budowie, co umożliwia rozróżnienie tych związków na widmie mas [45]. Oprócz zmiany rodzaju jonów reakcyjnych użytych do jonizacji obojętnych cząsteczek, innym rozwiązaniem w zakresie rozdzielania związków izobarycznych może być zastosowanie analizatora w postaci pułapki jonowej (PTR-IT-MS) [50] lub sprzężenie chromatografii gazowej ze spektrometrią PTR-MS (GC-PTR-MS) [51]. W Tabeli 4 przedstawiono przykłady związków występujących w powietrzu atmosferycznym zidentyfikowane w dotychczas prowadzonych badaniach z wykorzystaniem techniki PTR-MS.

Tabela 4 Przykłady związków chemicznych obecnych w próbkach powietrza atmosferycznego oznaczane z zastosowaniem techniki PTR-MS.

grupa związków chemicznych	nazwa związku chemicznego	numer CAS	wzór sumaryczny	powinowactwo do protonu [kJ/mol] [47,52,53]	lit.
alkohole	metanol	67-56-1	CH_3OH	755	[54–57]
	n-butanol	71-36-3	C_4H_9OH	789	[58]
	heksanol	111-27-3	$C_6H_{13}OH$	799	[59]
	2-metylo-3-buten-2-ol	115-18-4	C_5H_9OH	-	[60,61]
aldehydy	metanal	50-00-0	$HCHO$	713	[62]
	acetaldehyd	75-07-0	CH_3CHO	769	[54,57]
	heksanal	66-25-1	$C_5H_{11}CHO$	-	[63]
	heptanal	111-71-7	$C_6H_{13}CHO$	-	[63]
	nonanal	124-19-6	$C_8H_{17}CHO$	-	[63]
ketony	aceton	67-64-1	CH_3COCH_3	812	[54,55,57]
	keton metylowo - etylowy	78-93-3	$CH_3COC_2H_5$	827	[54,64,65]
	keton etylowinylowy	1629-58-9	$C_2H_5COCH=CH_2$	-	[63]
	keton izobutylowo - metylowy	108-10-1	$C_4H_9COCH_3$	-	[66]
	keton metylowinylowy	78-94-4	$CH_3COCH=CH_2$	835	[61]
	heksanon	591-78-6	$C_4H_9COCH_3$	-	[67]
kwasy karboksylowe	kwas metanowy	64-18-6	$HCOOH$	748	[68,69]
	kwas octowy	64-19-7	CH_3COOH	784	[54,62,64]
	kwas propanowy	79-09-4	C_2H_5COOH	797	[70]
	kwas butanowy	107-92-6	C_3H_8COOH	-	[70]
nitryle	akrylonitryl	107-13-1	C_2H_3CN	785	[58]
	acetonitryl	75-05-8	CH_3CH	779	[54,55,71,72]
lotne związki siarkoorganiczne	siarczek dimetylu	75-18-3	$(CH_3)_2S$	831	[73,74]

	siarkowodór	7783-06-4	H_2S	705	[65,70]
węglowodory aromatyczne	benzen	71-43-2	C_6H_6	750	[54,55,57,64,75,76]
	toluen	108-88-3	$C_6H_5CH_3$	784	[54,55,57,64,75–77]
	fenol	108-95-2	C_6H_5OH	817	[78]
	indol	120-72-9	$C_6H_4C_2H_2N$	933	[70]
	4-metylofenol	106-44-5	$C_6H_4(CH_3)OH$	814	[34]
aminy	dimetyloamina	124-40-3	$(CH_3)_2NH$	929	[70]
	trimetyloamina	75-50-3	$(CH_3)_3N$	949	[70]
dieny	1,3-butadien	106-99-0	$CH_2CHCHCH_2$	782	[79]
	izopren	78-79-5	$CH_2C(CH_3)CHCH_2$	826	[60,67]
terpeny	limonen	7705-14-8	$CH_3C_6H_8C(CH_3)CH_2$	-	[61]
	α-pinen	80-56-8	$CH_3C_6H_5CH_2(CH_3)_2$	-	[67]
	camfen	79-92-5	$CH_2C_6H_6CH_2(CH_3)_2$	-	[80]

Przeprowadzenie analizy jakościowej i ilościowej odorantów obecnych w powietrzu atmosferycznym może stanowić podstawę do oszacowania wpływu obecności tych związków na zapachowy charakter ich mieszaniny. Znajomość stężeń poszczególnych związków chemicznych obecnych w próbkach powietrza atmosferycznego umożliwia wyznaczenie parametru określającego teoretyczne stężenie zapachowe nazywane współczynnikiem aktywności zapachowej (OAV) [81]. Parametr ten wyliczany jest jako suma stosunków stężeń poszczególnych związków chemicznych obecnych w powietrzu atmosferycznym do ich indywidualnych progów wyczuwalności zapachowej, zgodnie z przedstawionym wzorem:

$$OAV = \sum_{i=1}^{n} \frac{c_i}{OT_i} \quad (1)$$

gdzie:

OAV – współczynnik aktywności zapachowej [ou/m^3]

c_i – stężenie substancji *i* [mg/m^3]

OT_i – próg wyczuwalności zapachowej substancji *i* [mg/ou]

Określenie teoretycznego stężenia zapachowego daje możliwość zobrazowania stopnia uciążliwości zapachowej na przyjętym obszarze poprzez wyznaczenie teoretycznego stężenia zapachowego dla próbek powietrza atmosferycznego pobranych z różnych lokalizacji w założonym czasie. Określenie korelacji pomiędzy teoretycznymi stężeniami zapachowymi a składem chemicznym próbek powietrza atmosferycznego (rodzajem obecnych związków oraz ich stężeniami) umożliwia wytypowanie tych związków, które mogą mieć największy wpływ na siłę odczuwanego zapachu [82]. Podejście to wykazuje się względnie wysoką powtarzalnością i odtwarzalnością uzyskiwanych wyników w porównaniu do technik olfaktometrycznych. Podstawową wadą tego podejścia jest jednak brak możliwości scharakteryzowania w sposób holistyczny wielu ważnych w punktu widzenia zjawiska uciążliwości zapachowej właściwości mieszanin zapachowych – intensywności zapachowej oraz jakości hedonicznej [83].

Wyznaczanie parametru OAV wydaje się być dobrym uzupełnieniem wyników uzyskanych technikami olfaktometrycznymi.

2.2.2. Techniki olfaktometryczne

Techniki instrumentalne powszechnie wykorzystywane do oznaczania stężeń poszczególnych odorantów obecnych w powietrzu atmosferycznym stanowią wartościowe narzędzie analityczne. Podstawowym ograniczeniem takiego podejścia jest jednak brak możliwości subiektywnego scharakteryzowania najważniejszych cech zapachu, takich jak intensywność zapachu, jakość hedoniczna czy przede wszystkim stężenie zapachowe. Wyznaczając tzw. teoretyczne stężenie zapachowe nie można odzwierciedlić, w sposób kompleksowy, wszystkich oddziaływań synergistycznych lub antagonistycznych związków zapachowych względem siebie. Ograniczenia technik instrumentalnych stanowią o sile technik sensorycznych, wśród których wiodącą rolę pełnią techniki olfaktometryczne: olfaktometria dynamiczna oraz terenowa [17,84].

Olfaktometria dynamiczna stanowi jedno z najczęściej wykorzystywanych rozwiązań w zakresie technik sensorycznych, umożliwiające określenie stężenia zapachowego, wyrażanego w europejskich jednostkach zapachowych na metr sześcienny (ou_E/m^3). Tak przedstawione stężenie określa stopień rozcieńczenia wonnej próbki gazowej strumieniem bezwonnego powietrza, konieczny do osiągnięcia tzw. progu wyczuwalności zapachowej [85]. Szczegółowe informacje dotyczące zasady oznaczania stężenia zapachowego metodą olfaktometrii dynamicznej zostały określone w europejskiej normie PN - EN 13725:2007: „Jakość powietrza. Oznaczanie stężenia zapachowego metodą olfaktometrii dynamicznej". Dokument ten stanowi jedyny przykład ujednoliconego uregulowania prawnego dotyczącego metodyki badań jakości powietrza z uwzględnieniem ich właściwości zapachowych. Na tle innych krajów Unii Europejskiej (np. Niemcy, Francja, Holandia, Wielka Brytania) czy też państw spoza UE (USA, Japonia, Korea Płd.) Polska wyraźnie odstaje pod względem istniejących aktów prawnych, dotyczących problemu uciążliwości zapachowej. W wielu przypadkach wprowadzane są jedynie różnego rodzaju przewodniki lub też poradniki, zawierające odniesienia do innych przepisów prawa w nieznacznym stopniu odnoszącym się do zagadnień związanych z ograniczaniem emisji zanieczyszczeń powietrza atmosferycznego. Sytuacja ta ma miejsce pomimo licznych prób wprowadzania odpowiednich zapisów prawnych, regulujących poziom emisji substancji złowonnych do otoczenia [86].

W trakcie prowadzenia oznaczeń techniką olfaktometrii dynamicznej ważny jest reprezentatywny charakter osób biorących udział w oznaczeniach. Umożliwia to uzyskanie wyniku zbliżonego do średniej uzyskanej dla licznej grupy osób oceniających zapach próbek. Najkorzystniejszym rozwiązaniem byłoby zaangażowanie w badania znacznej ilości osób, jednakże wymagałoby to dużego nakładu czasowego oraz finansowego. Większość obecnie dostępnych urządzeń przystosowana jest do jednoczesnego oceniania danej próbki powietrza przez 4-6 osób, choć dostępne są również modele 8-stanowiskowe [14]. Każda z osób uczestnicząca w badaniach powinna spełniać określone warunki. Jednym z najistotniejszych jest stała i niezmienna w czasie pomiaru wrażliwość na zapach przyjętego wzorca, jakim jest wodny roztwór n-butanolu. Członkowie zespołu oceniającego zapach na 30 minut przed prowadzeniem ocen powinni wstrzymać się od spożywania jakichkolwiek posiłków, przyjmowania płynów za wyjątkiem wody, palenia wyrobów tytoniowych, żucia gumy oraz stosowania wonnych preparatów kosmetycznych. Wymagania te związane są ze zmniejszeniem ryzyka zaburzenia percepcji zapachu. W trakcie przeprowadzania ocen wskazane jest zachowanie skupienia a także unikanie porozumiewania się między panelistami tak, aby odpowiedzi można było uznać za w pełni niezależne [87].

Istotną rolę w przeprowadzaniu ocen olfaktometrycznych odgrywają warunki panujące w laboratorium. Mogą one w znacznym stopniu wpływać na charakter odczuwanego zapachu. Dlatego też wymagane jest aby miejsce to było przyjemne i bezwonne. Należy unikać wszelkich możliwych źródeł emisji związków zapachowych, związanych z wyposażeniem laboratorium – zastosowane materiały konstrukcyjne, pokrycia ścian, podłóg i mebli. Miejsce to powinno być dobrze wentylowane, tak aby zminimalizować ryzyko interakcji zapachowych związanych z obecnością wonnych zanieczyszczeń powietrza obecnych wewnątrz pomieszczenia. Optymalna temperatura powietrza panująca w laboratorium powinna wynosić 25°C; wahania wobec tej wartości powinny mieścić się w zakresie ±3°C. Negatywny wpływ na wynik pomiarów może również wywierać hałas lub nadmierne działanie promieni słonecznych. Wskazane jest aby członkowie zespołu oceniającego zapach na 15 minut przez rozpoczęciem ocen mogli przebywać w laboratorium celem przystosowania się do warunków w nim panujących [88,89].

W trakcie przeprowadzania ocen olfaktometrycznych badana próbka, pobrana uprzednio do worka wykonanego z materiału odpornego na adsorpcję związków zapachowych, jest rozcieńczana strumieniem bezwonnego powietrza. Celem usunięcia wszelkich zanieczyszczeń w tym cząstek stałych, powietrze przed doprowadzeniem do olfaktometru oczyszczane jest na filtrach wykonanych z węgla aktywnego [90]. Początkowe rozcieńczenie próbki powinno być na tyle duże, aby osoba oceniająca nie była w stanie stwierdzić w niej obecności związków zapachowych. W zależności od modeli olfaktometrów kolejne rozcieńczenia uzyskiwane są manualnie lub automatycznie. Pomiar trwa do momentu aż osoba oceniająca zapach próbki wskaże przy którym rozcieńczeniu po raz pierwszy była w stanie wyczuć jakikolwiek zapach próbki. Stężenie zapachowe jest najczęściej obliczane jako średnia geometryczna wartości rozcieńczeń uzyskanych dla każdego z panelistów [91,92].

Dzięki zastosowaniu techniki olfaktometrii dynamicznej możliwe jest oszacowanie stężeń zapachowych z poszczególnych źródeł emisji. Na podstawie zebranych danych możliwe jest określenie całkowitej emisji odorów na danym obszarze oraz oszacowanie udziałów poszczególnych obiektów w całkowitej emisji, oszacowanie zakresu oddziaływania związków zapachowych emitowanych na badanym obszarze bądź wybranego obiektu, a także wyznaczenie stref występowania zjawiska uciążliwości zapachowej [93,94]. W celu uzyskania takich informacji konieczne jest jednak zastosowanie narzędzi matematycznych umożliwiających prognozowanie zmian stężeń poszczególnych odorantów w zależności od stopnia zabudowania oraz ukształtowania terenu, a także zmieniających się w trakcie prowadzenia pomiarów warunków atmosferycznych, w tym kierunku i siły wiatru, temperatury oraz wilgotności powietrza [10].

Technika olfaktometrii dynamicznej jest obecnie powszechnie stosowana w celu określana źródeł emisji związków zapachowych oraz poziomu ich emisji. W niektórych przypadkach jednak rozwiązanie to nie umożliwia uzyskania zadowalających wyników, np. w przypadku niewielkich stężeń. Kolejnym ograniczeniem techniki olfaktometrii dynamicznej jest konieczność pobierania próbek powietrza i transportowania ich do laboratorium. Wpływa to na wydłużenie czasu pojedynczego pomiaru oraz ryzyko utraty części analitów w wyniku procesów adsorpcji wewnątrz worka. Trudno jest określić stężenia zapachowe zwłaszcza w przypadku zmienności emisji na danym obszarze [95]. W takich przypadkach korzystniejsze wydaje się być zastosowanie techniki olfaktometrii terenowej. Rozwiązanie to umożliwia scharakteryzowanie właściwości odorantów obecnych w powietrzu atmosferycznym w wyniku rozcieńczania strumienia badanego powietrza bezwonnym gazem (najczęściej powietrzem oczyszczanym na filtrach węglowych) [96]. Wśród obecnie stosowanych urządzeń używanych do pomiarów olfaktometrycznych, najczęściej wykorzystywany jest olfaktometr terenowy Nasal Ranger (St. Croix Sensory, USA). Urządzenie to (35,5 x 19 x 10 cm, masa 0,91 kg) składa się z dwóch wymiennych filtrów wykonanych z węgla aktywnego, zaworu regulującego natężenie przepływu powietrza nieoczyszczanego przez filtry (a więc zawierającego w swym składzie związki zapachowe), wymiennej maski umożliwiającej wdychanie powietrza przez olfaktometr oraz czujnika umożliwiającego kontrolę natężenia przepływu strumienia gazu przechodzącego przez urządzenie [97]. Zawór regulujący umożliwia wybranie jednej z 6 dostępnych pozycji stopnia rozcieńczenia wdychanego powietrza: 60, 30, 15, 7, 4, 2. Istnieje możliwość wykorzystania dodatkowego zaworu dostosowanego do większych stężeń odorantów w powietrzu, umożliwiającego uzyskanie większych rozcieńczeń. Zawór ten posiada następujące wartości rozcieńczenia: 600, 500, 400, 300, 200, 100. Dodatkowo na każdym z dwóch dostępnych zaworów istnieje również pozycja „ślepa próba” (powietrze przechodzi jedynie przez filtry, a więc wdychane przez panelistę jest całkowicie oczyszczane i pozbawione zanieczyszczeń, w tym związków zapachowych) [98]. Dokładność i powtarzalność uzyskanych wyników z zastosowaniem olfaktometru terenowego Nasal Ranger wynoszą odpowiednio $\pm 10\ \%$ oraz $\pm 5\ \%$ [99].

Zastosowanie olfaktometrów terenowych umożliwia identyfikację punktowych źródeł emisji odorów najbardziej uciążliwych sensorycznie na obszarach sąsiadujących z najważniejszymi emitorami zapachowych zanieczyszczeń powietrza. Olfaktometry mogą być wykorzystywane zarówno jako urządzenia pomiarowe w celach naukowych oraz w celu weryfikacji skarg ludności odnośnie obecności związków uciążliwych zapachowo na terenach mieszkalnych, położonych w sąsiedztwie potencjalnych emitorów tych związków [21]. W pomiarach olfaktometrycznych powinny uczestniczyć min. 4 przeszkolone uprzednio osoby. Ważnym z punktu widzenia reprezentatywności uzyskanych wyników jest kontrola wrażliwości węchowej z wykorzystaniem substancji wzorcowej, którą jest wodny roztwór n-butanolu [17]. W trakcie każdej z serii pomiarowych zadaniem panelistów jest określenie stosunku ilości powietrza oczyszczanego na filtrach do ilości powietrza omijającego filtry (D/T) odpowiadającego pierwszemu momentowi w których zapach rozcieńczanego powietrza jest wyczuwalny. Na podstawie zbioru tych wartości oblicza się indywidualne oszacowanie stężenia zapachowego zgodnie z następującymi wzorami:

$$Z_{TAK} = \left({}^{D}/_{T}\right)_{TAK} + 1 \tag{2}$$

gdzie:

Z_{TAK} – stopień rozcieńczenia, przy którym zapach był wyczuwalny

$(D/T)_{TAK}$ – stopień rozcieńczenia odpowiadający momentowi, w którym zapach był po raz pierwszy wyczuwalny

$$Z_{NIE} = \left({}^{D}/_{T}\right)_{NIE} + 1 \tag{3}$$

gdzie:

Z_{NIE} – stopień rozcieńczenia, przy którym zapach nie był wyczuwalny

$(D/T)_{NIE}$ – stopień rozcieńczenia odpowiadający momentowi, w którym zapach nie był wyczuwalny jednakże bezpośrednio poprzedzał rozcieńczenie $(D/T)_{TAK}$

$$Z_{ITE} = \sqrt{Z_{TAK} \times Z_{NIE}} \tag{4}$$

gdzie:

Z_{ITE} – ocena progu indywidualnego

Wartości stężenia zapachowego oblicza się jako średnią geometryczną ze zbioru n wszystkich oszacowań indywidualnych dla danego punktu pomiarowego, zgodnie z przedstawionym poniżej wzorem:

$$c_{od} = \sqrt[n]{\sum^{n} Z_{ITE}} \tag{5}$$

gdzie:

c_{od} - wartość stężenia zapachowego [ou/m^3]

n – liczba wszystkich oszacowań indywidualnych

Zastosowanie techniki olfaktometrii terenowej umożliwia przeprowadzanie bezpośredniej kontroli emisji związków zapachowych emitowanych z różnego typu instalacji przemysłowych i komunalnych. Badania takie mogą służyć sprawdzaniu prawidłowego funkcjonowania zakładów produkcyjnych z punktu widzenia ilości odorów emitowanych do otoczenia w trakcie pojedynczego cyklu produkcyjnego [100]. Olfaktometria terenowa posiada szereg zalet, wśród których najistotniejszymi są względnie niski koszt związany z zakupem aparatury (znacznie tańszej niż olfaktometry dynamiczne), prostota w użytkowaniu oraz możliwość określenia stężeń zapachowych w czasie rzeczywistym. Wśród najważniejszych wad tej techniki należy podkreślić brak rozwiązań legislacyjnych, jasno określających warunki wyboru osób uczestniczących w badaniach, sposobu prowadzenia pomiarów oraz interpretacji uzyskanych wyników. Optymalnym rozwiązaniem w zakresie przygotowania osób uczestniczących w badaniach olfaktometrycznych byłoby przeprowadzenie w warunkach laboratoryjnych ocen wrażliwości zapachowej – do tego jednak konieczne byłoby dysponowanie olfaktometrami dynamicznymi, których koszt zakupu znacznie podniósłby wydatki związane z prowadzeniem badań. Alternatywnym rozwiązaniem jest oczywiście weryfikacja wrażliwości sensorycznej jedynie przy użyciu ogólnie przyjętych roztworów wzorcowych, np. wodnego roztworu n-butanolu [85,101]. W tabeli 5 przedstawiono przykłady stosowania technik olfaktometrycznych w badaniach środowiskowych.

Tabela 5 Przykłady stosowania technik olfaktometrycznych w badaniach środowiskowych.

technika	**źródło emisji**	**lit.**
olfaktometria dynamiczna	oczyszczalnia ścieków	[84,100,102]
	hodowla trzody chlewnej	[70,87,96,103]
	składowisko odpadów	[32,104–106]
	kompostownia	[107]
	zakłady utylizacji odpadów	[108]
olfaktometria terenowa	oczyszczalnia ścieków	[36,95,100,109,110]
	składowisko odpadów	[8,21]
	obszar wokół torów kolejowych	[111]

3. Osady ściekowe jako źródło emisji odorów

3.1. Powstawanie osadów ściekowych

Oczyszczalnie ścieków są jednymi z najważniejszych typów instalacji, stanowiących zespół urządzeń, aparatów i pomieszczeń, których zadaniem jest dostosowanie jakości dostarczanych do obiektu ścieków do powszechnie obowiązujących norm środowiskowych, odnoszących się do ponownego wykorzystania surowca odpadowego [112]. Poziom emisji związków zapachowych w trakcie funkcjonowania oczyszczalni ścieków jest silnie uzależniony od:

- rodzaju surowca dostarczanego na poszczególnych etapach jego obróbki, w tym obecności mikroorganizmów,
- tempa zachodzenia zmian o charakterze biochemicznym,
- warunków panujących w trakcie tych procesów,
- rozwiązań technologicznych i aparaturowych zastosowanych podczas poszczególnych procesów i operacji jednostkowych w trakcie oczyszczania ścieków [113,114].

Funkcjonowanie oczyszczalni ścieków nierozerwalnie wiąże się z powstawaniem znacznych ilości osadów ściekowych mimo, iż stanowią one zwykle jedynie 1-2% objętości oczyszczonych ścieków [115]. Dla przykładu w Stanach Zjednoczonych istniejące oczyszczalnie ścieków generują w skali roku ponad 6,5 mln ton suchej masy, w Chinach ok. 3 mln ton, natomiast w Japonii oraz w Niemczech ok. 2 mln ton. Biorąc pod uwagę dynamicznie postępujący rozwój gospodarczy i ekonomiczny w wielu krajach na całym świecie, szacuje się, że ilość osadów ściekowych w najbliższych latach będzie wzrastać [116].

Zróżnicowany charakter ścieków dopływających do oczyszczalni oraz rozmaite rozwiązania technologiczne wpływają na skład fizyko-chemiczny osadów ściekowych. Obecnie z uwagi na ekologiczne i toksykologiczne aspekty związane ze szkodliwością odpadów powstających w obiektach gospodarki komunalnej, coraz większą uwagę poświęca się substancjom chemicznym powstającym w wyniku biologicznego rozkładu materii organicznej. Jedną z ważniejszych grup związków obecnych w osadach ściekowych są lotne związki organiczne, w tym związki wykazujące właściwości zapachowe [117]. W literaturze najczęściej wymienianymi grupami związków wchodzącymi w skład gazowych mieszanin zapachowych powstających w oczyszczalniach ścieków są alkohole, aldehydy, ketony, związki siarkoorganiczne, estry, związki azotowe, węglowodory alifatyczne i aromatyczne[118].

3.2. Metody przetwarzania i zagospodarowania osadów ściekowych

Pomimo licznych prac modernizacyjnych prowadzonych w ostatnich latach na terenach oczyszczalni ścieków komunalnych i przemysłowych, kwestia zagospodarowania osadów ściekowych stanowi wciąż poważny problem. W związku z rozporządzeniem wydanym w 2016 roku, wprowadzającym zakaz składowania komunalnych osadów ściekowych na terenie składowiska odpadów, zainteresowanie pozostałymi możliwymi metodami zagospodarowania osadów ściekowych znacząco wzrosło [119]. Wybór optymalnej metody uzależniony jest od wielu czynników takich jak: redukcja objętości przetwarzanych osadów, zmniejszenie ilości patogenów, obniżenie ładunku węgla organicznego oraz maksymalizacja stopnia wykorzystania substancji biogennych obecnych w osadach ściekowych przy zachowaniu wszelkich wymogów związanych z bezpieczeństwem sanitarnym i chemicznym [120,121]. Uwzględnienie możliwie jak największej ilości parametrów stwarza możliwości opracowania metody korzystnej zarówno pod względem ekonomicznym jak i ekologicznym. Obecnie do najbardziej popularnych metod zagospodarowania osadów ściekowych należą: wykorzystanie w rolnictwie, uprawa roślin nieprzeznaczonych do spożycia, rekultywacja gruntów w celu dostosowania ich do określonych potrzeb, wykorzystanie w budownictwie, odzysk surowców oraz wytwarzanie adsorbentów na bazie osadów ściekowych [122].

W przypadku większości z wymienionych powyżej metod zagospodarowania osadów, konieczne jest ich wcześniejsze przetworzenie. Wśród najczęściej stosowanych operacji jednostkowych stosowanych w tym celu zalicza się odwadnianie, kompostowanie i stabilizację. W przypadku wykorzystania w rolnictwie operacje te mają na celu zmniejszenie ryzyka niekontrolowanego uwalniania substancji chemicznych do gleb oraz wód gruntowych [123]. W przypadku stosowania przetworzonych osadów ściekowych w budownictwie daje to możliwości uzyskania materiału o bardzo dobrych właściwościach mechanicznych i wytrzymałościowych [124,125].

Odwadnianie osadów jest procesem usuwania wody z osadu w celu zmniejszenia jego objętości. Woda wolna i woda kapilarna usuwane są w procesie zagęszczania (naturalnego lub mechanicznego) natomiast woda adsorpcyjna usuwana jest w trakcie suszenia [126]. Kompostowaniu poddaje się osady poddane wcześniej procesom odwodnienia, zmieszane ze słomą lub trocinami. Odpowiedni dobór substratu dodawanego do osadu bardzo często decyduje o jakości uzyskiwanego kompostu [127]. Proces kompostowania prowadzony jest najczęściej w warunkach tlenowych, w układzie pryzmowym. We wszystkich kompostowniach zalecane jest prowadzenie procesu dezodoryzacji strumienia gazu stosowanego do napowietrzania pryzm z uwagi na ryzyko przedostawania się związków uciążliwych zapachowo do otoczenia [128,129]. Stabilizacja osadów ściekowych może być prowadzona na drodze procesów biologicznych, chemicznych lub termicznych. Głównymi założeniami prowadzenia procesu stabilizacji osadów jest przygotowanie ich do dalszego zagospodarowania poprzez obniżenie zawartości związków organicznych, patogenów, zmniejszenie ich całkowitej objętości oraz zmniejszenie podatności na zagniwanie, co również wpływa na zmniejszenie potencjalnej uciążliwości zapachowej związanej z dalszym przetwarzaniem osadów ściekowych [130].

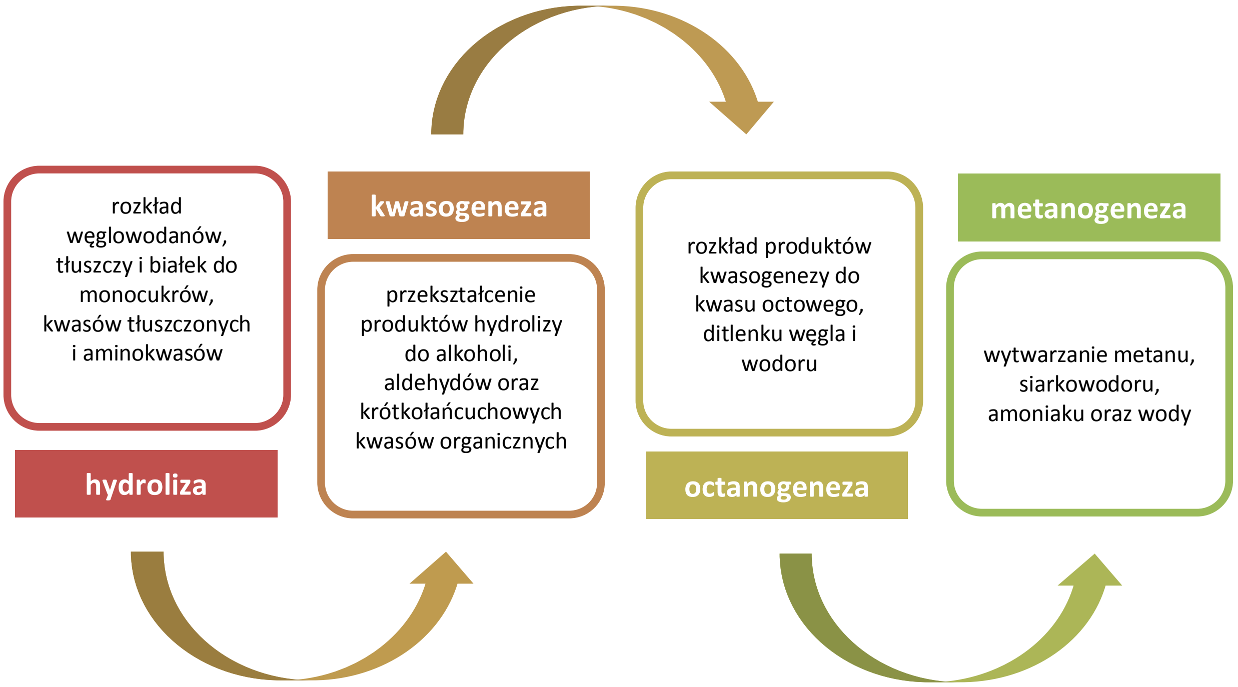
Na przestrzeni ostatnich kilkunastu lat obserwuje się znaczący wzrost zainteresowania termicznymi metodami przekształcania osadów. Spośród obecnie dostępnych metod najczęściej wymienia się: spalanie, współspalanie z innymi mediami energetycznymi, takimi jak węgiel kamienny lub ropa naftowa oraz procesy alternatywne (piroliza, zgazowanie oraz procesy hybrydowe) [131]. Niewątpliwą przewagą metod termicznego zagospodarowania osadów, prowadzonych w temperaturach powyżej 700°C w porównaniu do biologicznych i chemicznych metod zagospodarowania jest niemal całkowite zmineralizowanie związków organicznych. Pod wpływem działania wysokiej temperatury ulegają one przekształceniom do prostych związków nieorganicznych (głównie ditlenku węgla i wody) [132]. Podczas projektowania instalacji do termicznego przekształcania osadów należy jednak brać pod uwagę konieczność usuwania licznych zanieczyszczeń gazowych powstających w trakcie operacji wysokotemperaturowych, głównie tlenków siarki, azotu oraz węgla. Ich ilość może być stosunkowo duża, zwłaszcza w przypadku zbyt niskiej temperatury spalania osadów (<700°C). Obróbka wysokotemperaturowa charakteryzuje się również znaczną redukcją objętości i masy przetwarzanych osadów [133].

W przypadku stosowania chemicznych metod stabilizacji najczęściej stosowane są środki silnie alkalizujące bądź zakwaszające, które powodują skuteczne zniszczenie mikroorganizmów chorobotwórczych, patogenów oraz pasożytów [134]. Jednym z powszechnie stosowanych środków dezynfekcyjnych jest tlenek lub wodorotlenek wapnia. Jego dodatek powodujący wzrost pH do ok 11-12 powoduje niszczenie struktur bakterii i wirusów po godzinnej ekspozycji. Mieszanie osadu z wapnem jest bardzo korzystne w przypadku dalszego zagospodarowania osadów w rolnictwie. Uzyskuje się w ten sposób zmniejszenie ilości wapna jakie należy dostarczyć bezpośrednio do gleby [135].

Jedną z najczęściej stosowanych form stabilizacji biologicznej osadów ściekowych jest fermentacja beztlenowa (nazywana również fermentacją metanową) z jednoczesnym odzyskiem biogazu, którego głównym składnikiem jest metan. Metoda ta cieszy się coraz większą popularnością ze względu na możliwość wytwarzania w trakcie tego procesu biogazu stanowiącego źródło energii odnawialnej [136]. W zależności od sposobu prowadzenia procesu fermentacji, możliwe jest wytworzenie biogazu o zawartości do 70% metanu [137]. W zależności od temperatury prowadzenia procesy wyróżnia się fermentację:

- psychrofilową (T<20°C);
- mezofilową (T=30-38°C);
- termifilową (T=45-58°C).

Podstawowymi parametrami wpływającymi na przebieg procesu fermentacji, a co z tym idzie jakości otrzymywanego osadu oraz biogazu są ilość i częstotliwość doprowadzanego osadu surowego, intensywność mieszania, odczyn, zawartość lotnych kwasów tłuszczowych oraz zasadowość [138]. Na rys. 2 przedstawiono schemat tego procesu z uwzględnieniem 4 głównych jego faz: hydrolizy, kwasogenezy, octanogenezy i metanogeneza [139].

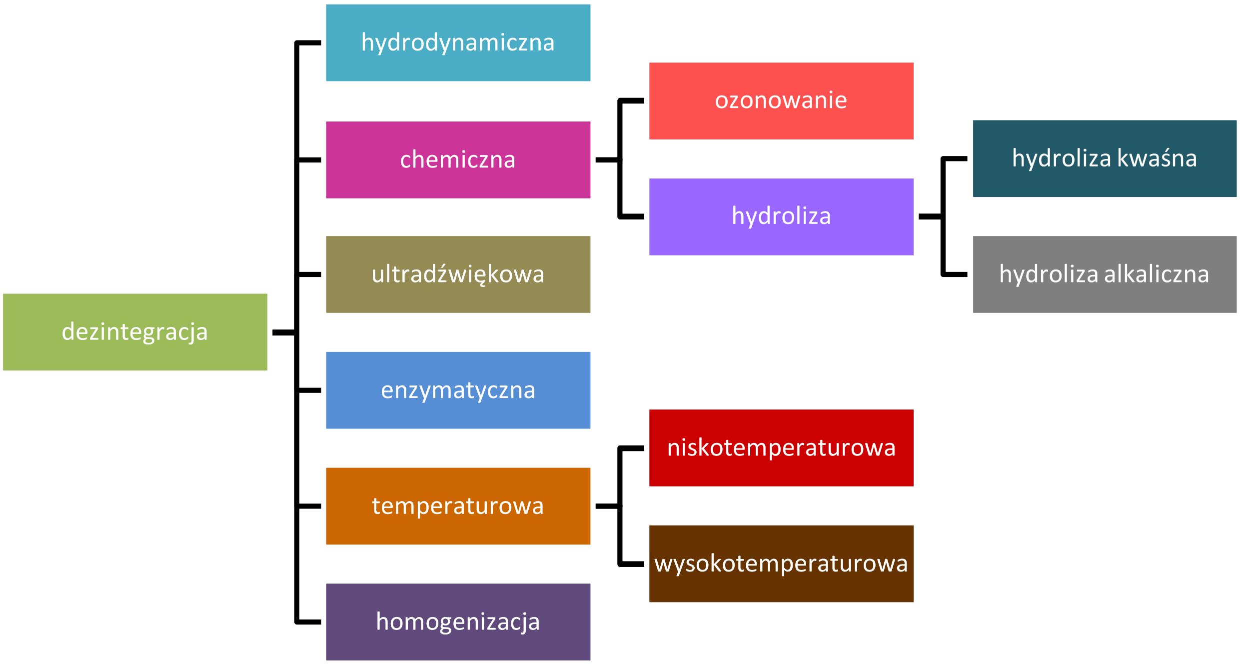


Rysunek 2 Przebieg procesu fermentacji metanowej.

W celu zwiększenia ilości biogazu produkowanego w trakcie procesu fermentacji beztlenowej, oczyszczalnie ścieków wybierają najczęściej jedno z dwóch możliwych rozwiązań:

- odpowiedni dobór substratów wprowadzanych do komór fermentacyjnych;
- wstępne przygotowanie wsadu w celu zwiększenia dostępności substratów dla bakterii uczestniczących w procesie fermentacji metanowej, a przede wszystkim tych determinujących tempo przemian podczas acetogenezy i metanogenezy.

W pierwszym z wymienionych przypadków proces fermentacji określany jest mianem kofermentacji – do wsadu dodawany jest koferment, którego dodatek zwiększa efektywność powstawania biogazu. Najczęściej stosowanymi kofermentami są odpady pochodzenia rolniczego, np. gnojowica, wywar buraczany [140]. W drugim z wymienionych przypadków substrat docelowo przeznaczony do procesu fermentacji poddawany jest procesowi dezintegracji, polegającego na zmianie właściwości fizyko-chemicznych dezintegrowanego medium poprzez dostarczenie dodatkowej porcji energii. Podczas tego procesu następuje zniszczenie struktury komórkowej substratów przez co zwiększa się jego podatność na dalszy rozkład biologiczny [130]. Prowadzenie procesu dezintegracji osadów ściekowych wiąże się nie tylko ze zwiększeniem efektywności produkcji biogazu. Przy właściwie dobranych parametrach procesu możliwe jest również zwiększenie zdolności do odwadniania osadu pofermentacyjnego, co zmniejsza ilość powstającego osadu. Możliwe jest również zmniejszenie zużycia polielektrolitu, co istotnie wpływa na aspekty finansowe związane z przetwarzaniem osadów [141]. Na rysunku 3 przedstawiono najczęściej stosowane rozwiązania w zakresie dezintegracji osadów ściekowych.



Rysunek 3 Główne typy procesów dezintegracji osadów ściekowych.

3.3 Ocena oddziaływania zapachowego osadów ściekowych

Kwestia dotycząca zagospodarowania i przetwarzania osadów ściekowych stanowi na tyle poważny problem, iż w wielu krajach wprowadza się szereg regulacji prawnych w tym zakresie. Jednym z najważniejszych dokumentów jest Dyrektywa Parlamentu Europejskiego i Rady 2008/98/WE z dnia 19 listopada 2008 r. zawierająca wytyczne dotyczące działań jakie należy podejmować w związku ze zmniejszaniem negatywnego wpływu na środowisko poprzez zapobieganie i zmniejszanie wytwarzanej ilości odpadów, w tym osadów ściekowych [142]. Obowiązujące obecnie akty prawne w tym m.in.:

- Dyrektywa Rady 86/278/EWG z dnia 12 czerwca 1986 roku wprowadzająca przepisy regulujące stosowanie osadów ściekowych w rolnictwie,
- Rozporządzenie Ministra Rozwoju z dnia 21 stycznia 2016 roku określające wymagania dotyczące prowadzenia termicznego przekształcania odpadów
- Dyrektywa Parlamentu Europejskiego i Rady 2009/28/WE z dnia 23 kwietnia 2009 roku określająca wymagane do osiągnięcia poziomy energii pochodzące z odnawialnych źródeł energii, w tym z biomasy, do której zaliczane są również osady ściekowe,

nie odnoszą się jednak do problemu wpływu zawartości związków zapachowych obecnych w osadach ściekowych na sposób ich przetwarzania oraz późniejszego zagospodarowania [120]. Problem ten może wynikać z braku odpowiednich regulacji prawnych w zakresie jakości powietrza atmosferycznego i dopuszczalnych stężeń zapachowych wokół głównych źródeł emisji odorów [86,143]. Dyrektywy wydawane przez Unię Europejską opierają się głównie na systemie ostrzegania przed możliwymi konsekwencjami związanymi w niewłaściwym przetwarzaniem i zagospodarowywaniem osadów. Obowiązujące dokumenty są niezbędne w dobie intensywnego rozwoju urbanistycznego i związanego z nim wzrostem ilości gospodarstw domowych generujących coraz większe ilości ścieków. Oprócz rozwiązań legislacyjnych wprowadzanych przez Unię Europejską, kraje członkowskie zobowiązały się do wprowadzania własnych aktów prawnych, które w niektórych przypadkach są znacznie bardziej rygorystyczne niż te, wydawane przez Unię Europejską. Sytuacja taka wiąże się również ze stopniowym wycofywaniem dotychczas obowiązujących aktów prawnych w poszczególnych krajach, a to niesie ze sobą ryzyko wystąpienia czasowych luk prawnych w zakresie dopuszczalnych norm emisji dla danego typu zanieczyszczeń [124].

Niewątpliwie kwestią problematyczną w Polsce jest brak regulacji prawnych w zakresie monitorowania dopuszczalnych ilości związków zapachowych mogących przedostawać się do środowiska. Prace nad takim dokumentem (określanym mianem „ustawy odorowej”) trwają już ponad 10 lat i niestety brak jest konkretnych działań, mogących dawać nadzieję na jej wprowadzenie. Odnosząc się do regulacji prawnych wydawanych przez Unię Europejską warto zwrócić uwagę, iż w Dyrektywie Parlamentu Europejskiego z dnia 21 maja 2008 roku w sprawie jakości powietrza i czystszego powietrza dla Europy nie pojawia się nawet ani słowo „odór” ani „zapach”. Dokument ten odnosi się do obecności w powietrzu atmosferycznym głównie takich substancji jak: tlenki azotu, siarki i węgla, benzenu, ozonu, pyłu zawieszonego PM_{10}, $PM_{2,5}$ oraz ołowiu.

Wobec braku podstaw prawnych uwzględniających dopuszczalny poziom emisji odorów do powietrza atmosferycznego, trudno jest o przeprowadzenie oceny oddziaływania zapachowego operacji związanych z przetwarzaniem i zagospodarowaniem osadów ściekowych. Konieczne jednak wydaje się prowadzenie badań w celu wykazania istoty tego zagadnienia i wskazania dokładnych obszarów, w których należy zintensyfikować prace badawcze, aby stworzyć podstawę do wprowadzenia odpowiednich regulacji prawnych, w których uwzględnionoby wpływ związków zapachowych obecnych w osadach ściekowych na stan środowiska, w tym również na zdrowie człowieka.

II CZĘŚĆ DOŚWIADCZALNA

4. Cel i zakres badań

4.1. Cel prowadzonych badań

Głównym założeniem rozprawy doktorskiej było **scharakteryzowanie zapachowego oddziaływania osadów ściekowych powstających w trakcie oczyszczania ścieków komunalnych**.

Realizacja głównego założenia rozprawy doktorskiej obejmowała następujące cele badawcze:

- porównanie stężeń zapachowych wyznaczanych metodą olfaktometrii terenowej oraz teoretycznych stężeń zapachowych wyznaczanych na podstawie analiz instrumentalnych (cel badawczy nr 1);
- wytypowanie potencjalnych wyróżników poszczególnych typów osadów ściekowych powstających w trakcie oczyszczania ścieków (cel badawczy nr 2);
- ocenę potencjału odorowego ustabilizowanych osadów ściekowych w trakcie procesu ich starzenia (cel badawczy nr 3);
- charakterystykę ryzyka zmian zdrowotnych u ludzi związanego z ekspozycją na związki zapachowe uwalniane w trakcie różnych procesów przeprowadzanych w oczyszczalni ścieków w tym obejmujących przetwarzanie osadów ściekowych (cel badawczy nr 4);
- opracowanie i walidację metodyki, umożliwiającej oznaczanie lotnych związków aromatycznych wykazujących właściwości zapachowe, uwalnianych z osadów ściekowych z wykorzystaniem techniki HS-GC-MS/MS (cel badawczy nr 5);
- wykorzystanie sieci neuronowych oraz drzew decyzyjnych w celu przewidywania stopnia uciążliwości zapachowej osadów pofermentacyjnych (cel badawczy nr 6).

Realizacja przedstawionych celów badawczych została opisana w publikacjach załączonych do niniejszej rozprawy doktorskiej, omówionych w rozdziałach 5.1 – 5.6.

4.1. Materiał badawczy

Przedmiotem prowadzonych badań były próbki osadów ściekowych, pobierane z różnych etapów ich przetwarzania oraz próbki powietrza atmosferycznego pobierane zarówno z terenu oczyszczalni ścieków jak i terenów z nią sąsiadujących. Realizacja zaplanowanych badań była możliwa dzięki uprzejmości 4 oczyszczalni ścieków położonych w województwie pomorskim:

- Oczyszczalnia Ścieków "Gdańsk – Wschód";
- Grupowa Oczyszczalnia Ścieków "Dębogórze";
- Oczyszczalnia Ścieków w Starogardzie Gdańskim;
- Oczyszczalnia Ścieków w Swarzewie.

W przypadku realizacji zadań badawczych nr 1 i 4 materiał do badań stanowiły próbki powietrza atmosferycznego, pobierane w przyjętych do badań lokalizacjach pomiarowych, uwzględniających zarówno obszar na terenie oczyszczalni oraz tereny z nią sąsiadujące.

W przypadku realizacji zadań badawczych nr 2 oraz nr 3 próbki osadów ściekowych pobierano do wiader wykonanych z tworzywa sztucznego o pojemności 20 L i po szczelnym zamknięciu transportowano do laboratorium. Tak duże ilości materiału badawczego wynikały z wykorzystania w trakcie badań dynamicznej komory przepływowej. Próbki osadów przetransportowano w dniu ich pobierania do laboratorium Katedry Chemii Analitycznej Wydziału Chemicznego Politechniki Gdańskiej. Badania nad określaniem poziomów emisji związków zapachowych z pobranych próbek rozpoczęto w dniu ich pobierania i przetransportowania do laboratorium.

W przypadku realizacji zadań badawczych nr 5 oraz 6 próbki osadów ściekowych każdorazowo pobierano do szklanych butelek o pojemności 500 ml i zamykano szczelnie, w celu uniemożliwienia zachodzenia zmian w składzie frakcji lotnej. Butelki wypełniano w całości pobieranymi próbkami w celu zniwelowania ryzyka zmian w składzie w wyniku zachodzenia procesów w środowisku tlenowym. Uzyskiwany materiał badawczy transportowano w dniu pobierania do laboratorium Katedry Chemii Analitycznej Wydziału Chemicznego Politechniki Gdańskiej i przechowywano w warunkach chłodniczych (+4°C) do momentu rozpoczęcia prac związanych z bezpośrednim przygotowaniem próbek do analiz. Analizy przeprowadzano nie później niż 14 dni od dnia pobrania próbek z oczyszczalni ścieków.

4.2. Metodyka badawcza

W badaniach przeprowadzonych w ramach realizacji celów szczegółowych niniejszej pracy doktorskiej wykorzystywano nowoczesne techniki instrumentalne i sensoryczne: dwuwymiarową chromatografię gazową sprzężoną ze spektrometrią mas i analizą czasu przelotu jonów fragmentacyjnych (GCxGC-TOF-MS), spektrometrię mas z jonizacją poprzez reakcję przeniesienia protonu (PTR-TOF-MS), chromatografię gazową sprzężoną z tandemową spektrometrią mas (GC-MS/MS) oraz olfaktometrię terenową. W przypadku badań prowadzonych z zastosowaniem GCxGC-TOF-MS próbki powietrza pobierano z wykorzystaniem rurek z wypełnieniem z postaci stałego sorbentu (Tenax TA) oraz urządzenia *Gas Sampling System* (GSS, Gerstel, Germany). Rozwiązanie to umożliwiało oznaczanie szerokiej gamy analitów występujących na bardzo niskich poziomach stężeń. Dobór sorbentu stosowanego w badaniach podyktowany był głównie informacjami zaczerpniętymi z literatury odnośnie oznaczania analitów z grupy lotnych związków organicznych występujących w powietrzu atmosferycznym [144,145]. Wprowadzanie analitów do układu chromatograficznego odbywało się z wykorzystaniem desorbera termicznego.

W trakcie prowadzenia badań z zastosowaniem techniki PTR-MS nie było konieczne przygotowanie próbek do analiz, gdyż aparatura ta umożliwia oznaczanie analitów w czasie rzeczywistym bez konieczności przygotowania próbek np. z zastosowaniem żmudnych i pracochłonnych operacji związanych z izolacją i wzbogacaniem analitów. W ramach zadania badawczego nr 3 wykorzystano połączenie dynamicznej komory przepływowej ze spektrometrem mas z jonizacją poprzez reakcję przeniesienia protonu. W przypadku stosowania dynamicznej komory przepływowej, stanowiącej osłonę w kształcie kopuły z otwartą podstawą, do jej wnętrza doprowadzany jest gaz o wysokiej czystości o znanym i ustalonym przepływie. Pod kopułą osłony ulega on wymieszaniu z mieszaniną związków zapachowych uwalnianych z badanych próbek znajdujących się we wnętrzu kopuły. W celu wyrównywania ciśnienia kopuła zawiera w sobie otwór odprowadzający powstającą mieszaninę gazową. Dzięki umieszczeniu dodatkowego otworu możliwe jest również połączenie dynamicznej komory przepływowej z innym urządzeniem (w przypadku realizacji celu badawczego nr 3 dynamiczną komorę przepływową połączono ze spektrometrem mas z jonizacją poprzez reakcję przeniesienia protonu, natomiast w przypadku realizacji celu badawczego nr 2 dodatkowy przewód odprowadzający wykorzystano jako wlot do rurki ze stałym sorbentem z zastosowaniem którego pobierano anality do analiz chromatograficznych).

5. Omówienie uzyskanych wyników

5.1. Realizacja celu badawczego nr 1

Podstawowym narzędziem stosowanym do oceny stopnia uciążliwości zapachowej związanej z funkcjonowaniem obiektów gospodarki komunalnej są techniki olfaktometryczne. Dzięki nim możliwe jest określenie stężenia zapachowego, odpowiadającego ilości odorantów w próbkach powietrza atmosferycznego. Wybrane modele olfaktometrów dynamicznych umożliwiają również wyznaczenie intensywności zapachowej oraz jakości hedonicznej próbek gazowych. W przypadku stosowania techniki olfaktometrii dynamicznej nie ma niestety możliwości scharakteryzowania składu chemicznego próbek. Istotnym ograniczeniem stosowania tej techniki są również kwestie ekonomiczne.

W ramach przeprowadzonych badań podjęto próbę wyznaczenia tzw. teoretycznych stężeń zapachowych w oparciu o wyniki analiz instrumentalnych przeprowadzonych z zastosowaniem techniki dwuwymiarowej chromatografii gazowej sprzężonej ze spektrometrią mas (GCxGC-MS) oraz o wartości literaturowe progów wyczuwalności zapachowej oznaczanych substancji. Próbki gazowe zawierające związki zapachowe pobierano za pomocą rurek z wypełnieniem w postaci stałego sorbentu typu Tenax TA w 4 punktach pomiarowych zlokalizowanych wokół dwóch zakładów przemysłowych i komunalnych zlokalizowanych w bardzo bliskim sąsiedztwie, tj. oczyszczalni ścieków Gdańsk – Wschód oraz pobliskiej Rafinerii grupy Lotos S.A. W tych samych lokalizacjach pomiarowych 4-osobowy zespół osób oceniających zapach uczestniczył w terenowych pomiarach olfaktometrycznych, w celu wyznaczenia stężeń zapachowych z użyciem olfaktometrów Nasal Ranger (St. Croix Sensory, USA). Uzyskane w ten sposób wyniki oznaczeń instrumentalnych i sensorycznych porównano ze sobą. Na ich podstawie stwierdzono, iż teoretyczne stężenia zapachowe różnią się od stężeń zapachowych, uzyskanych za pomocą techniki olfaktometrii terenowej. Główną przyczyną może być fakt, iż postrzeganie zapachu gazowej mieszaniny jako sumy stężeń zapachowych poszczególnych substancji nie uwzględnia takich zjawisk jak maskowanie lub wzmacnianie zapachu, co w konsekwencji przyczynia się do różnic w uzyskanych wynikach. Podejście instrumentalne w oznaczaniu stężeń zapachowych może jedynie stanowić uzupełnienie badań związanych uciążliwością zapachową wokół terenów zlokalizowanych w bezpośrednim sąsiedztwie najważniejszych źródeł emisji odorów, takich jak zakłady komunalne i przemysłowe.

Wyniki omówionych badań zostały przedstawione w pracy pt. *Determination of odour concentration by TD-GCxGC-TOF-MS and field olfactometry techniques*, opublikowanej w czasopiśmie *Monatshefte für Chemie - Chemical Monthly*, stanowiącej załącznik nr 1 do niniejszej rozprawy doktorskiej.

5.2. Realizacja celu badawczego nr 2

Osady ściekowe są jednym z głównych typów odpadów, powstających w trakcie oczyszczania ścieków. Stanowią one źródło wielu lotnych związków chemicznych, w tym związków mogących przyczyniać się do występowania zjawiska uciążliwości zapachowej zarówno na terenach oczyszczalni jak i w ich bezpośrednim sąsiedztwie. Z tego względu konieczne wydaje się opracowanie skutecznych rozwiązań metodycznych w zakresie ograniczenia emisji związków zapachowych. Ze względu na fakt, iż ich liczba jest stosunkowo duża, istotnym wydaje się zaproponowanie narzędzi analitycznych i statystycznych, umożliwiających wytypowanie kluczowych związków stanowiących potencjalne wyróżniki poszczególnych typów osadów ściekowych.

W trakcie prowadzonych badań wykorzystano technikę dwuwymiarowej chromatografii gazowej sprzężonej ze spektrometrią mas i analizą czasu przelotu jonów fragmentacyjnych (GCxGC-TOF-MS) w celu identyfikacji związków zapachowych uwalnianych z 4 typów osadów ściekowych (osad wstępny, osad nadmierny, osad przefermentowany oraz osad przefermentowany odwodniony) pobranych w dwóch oczyszczalniach ścieków, znajdujących się w woj. pomorskim. Pobieranie próbek powietrza możliwe było dzięki wykorzystaniu dynamicznej komory przepływowej, umożliwiającej określenie poziomu emisji związków zapachowych uwalnianych z badanych próbek osadów ściekowych oraz rurek z wypełnieniem w postaci stałego sorbentu typu Tenax TA. Dzięki zastosowaniu analizy wariancji możliwe było wytypowanie potencjalnych wyróżników próbek (1-propanol, 2-heksanon, toluen, o-ksylen, p-ksylen oraz lotne związki siarkoorganiczne: metanotiol, etanotiol, siarczek dimetylu, disiarczek dimetylu i disiarczek dietylu). Na podstawie wyznaczonych stężeń potencjalnych wyróżników badanych próbek oraz wartości literaturowych progów wyczuwalności zapachowej, możliwe było oszacowanie stężeń zapachowych dla 4 typów badanych osadów. Najwyższą wartość c_{od} uzyskano dla osadu wstępnego (634 ou/m^3), natomiast najniższą dla osadu nadmiernego, uzyskanego po biologicznym oczyszczaniu ścieków (136 ou/m^3). Zaproponowane podejście nie uwzględnia oczywiście wszystkich substancji mogących wpływać na rzeczywiste wartości stężeń zapachowych, natomiast stanowi niewątpliwie interesującą alternatywę dla pomiarów olfaktometrycznych, które zwłaszcza w przypadku stosowania techniki olfaktometrii dynamicznej wiążą się z względnie wysokimi kosztami aparaturowymi.

Wyniki przeprowadzonych badań zostały przedstawione w pracy pt. *Complementary use of GCxGC–TOF–MS and statistics for differentiation of variety in biosolid samples*, opublikowanej w czasopiśmie *Monatshefte für Chemie - Chemical Monthly*, stanowiącej załącznik nr 2 do niniejszej rozprawy doktorskiej.

5.3. Realizacja celu badawczego nr 3

Stabilizacja osadów ściekowych jest jednym z najczęściej stosowanych zabiegów mających na celu zmniejszanie negatywnego oddziaływania na środowisko osadów ściekowych powstających w trakcie oczyszczania ścieków. Większość oczyszczalni prowadzi ten proces w warunkach beztlenowych z odzyskiem metanu stanowiącego jedną z pro-ekologicznych form energii (fermentacja metanowa). Informacje zaczerpnięte z literatury wskazują, iż pomimo prowadzenia tego procesu, duża ilość związków chemicznych nadal pozostaje w osadach ściekowych, co znacząco ogranicza ich potencjalne zastosowanie np. w rolnictwie. W związku z tym konieczne jest dysponowanie rozwiązaniami metodycznymi, umożliwiającymi monitorowanie zmian stężeń tych substancji. Istotne jest również wyznaczenie zależności pomiędzy ich stężeniami a czasem przechowywania osadów (tj. okresem starzenia się osadów ściekowych).

W celu oszacowania zmian w składzie frakcji lotnej przefermentowanych osadów ściekowych poddanych procesowi starzenia, wykorzystano dynamiczną komorę przepływową w połączeniu ze spektrometrem mas z jonizacją poprzez reakcję przeniesienia protonu (PTR-MS). Rozwiązanie to umożliwiało szybką analizę próbek osadów ściekowych, bez konieczności ich wcześniejszego przygotowania w tym zużycia szkodliwych dla środowiska odczynników chemicznych. W celu przeprowadzenia badań pobrano próbki osadów ściekowych poddanych uprzednio procesowi fermentacji beztlenowej z dwóch oczyszczalni ścieków zlokalizowanych w woj. pomorskim. Zastosowanie przedstawionej aparatury umożliwiało monitorowanie zmian stężeń wybranych odorantów w trakcie starzenia się osadów ściekowych. Wykazano, że podczas tego procesu, stężenia poszczególnych odorantów ulegają zmianie. Stężenia części oznaczanych związków ulegały zwiększeniu w trakcie prowadzenia badań. Ich ilość - nawet po niemal miesiącu od dnia przeprowadzenia fermentacji - nadal może powodować zagrożenia dla środowiska. Konieczne jest więc dalsze przetwarzanie osadów ściekowych, w zależności od planowanego sposobu ich zagospodarowania.

Wyniki przeprowadzonych badań zostały przedstawione w pracy pt. *Monitoring of odors emitted from stabilized dewatered sludge subjected to aging using proton transfer reaction–mass spectrometry*, opublikowanej w czasopiśmie *Environmental Science and Pollution Research*, stanowiącej załącznik nr 3 do niniejszej rozprawy doktorskiej.

5.4. Realizacja celu badawczego nr 4

Oczyszczalnie ścieków komunalnych stanowią jedno z potencjalnych źródeł emisji związków zapachowych, mogących wpływać na pogorszenie stanu zdrowia osób stale tam przebywających, przede wszystkim ich pracowników. Stopień narażenia uzależniony jest od charakteru procesów przeprowadzanych w oczyszczalniach, ilości ścieków doprowadzanych do zakładu oraz od wielkości oczyszczalni. Badania dotyczące oceny ryzyka prowadzone są m.in. poprzez wyznaczanie współczynników rakotwórczego i nie-rakotwórczego ryzyka zdrowotnego w związku z ekspozycją na lotne związki chemiczne obecne w powietrzu atmosferycznym, zgodnie z metodyką zaproponowaną przez Agencję Ochrony Środowiska Stanów Zjednoczonych (US EPA).

W przeprowadzonych badaniach podjęto próbę wyznaczenia parametrów – ryzyka rakotwórczego (CR) oraz nie-rakotwórczego (HI) na podstawie analiz próbek powietrza pobranych z 4 lokalizacji pomiarowych (hala mechanicznego oczyszczania ścieków, obszar reaktorów biologicznych, pryzmy kompostowe zawierające pozostałości po mechanicznym oczyszczaniu ścieków oraz pryzmy kompostowe osadów ściekowych poddanych uprzednio procesowi fermentacji), znajdujących się na terenie jednej z oczyszczalni ścieków zlokalizowanej na terenie województwa pomorskiego. Analizę ilościową przeprowadzono z zastosowaniem techniki GCxGC-TOF-MS. W trakcie pobierania próbek powietrza wykorzystano rurki z wypełnieniem w postaci stałego sorbentu typu Tenax TA. Do wyznaczania parametrów CR oraz HI wykorzystano również dane dotyczące przyjętego czasu ekspozycji oraz częstości ekspozycji na substancje uwalniane w trakcie oczyszczania ścieków i przetwarzania osadów ściekowych. Przeprowadzono również analizy olfaktometryczne z wykorzystaniem techniki olfaktometrii terenowej przeprowadzone w tych samych punktach pomiarowych.

Na podstawie stężeń związków chemicznych oznaczonych w próbkach powietrza, możliwe było wyznaczenie parametrów CR oraz HI dla poszczególnych substancji oraz określenie wartości sumarycznych tych parametrów, odpowiadających sumie stężeń związków chemicznych oznaczanych w przyjętych lokalizacjach pomiarowych. Wartości sumaryczne parametru CR znajdowały się w zakresie $1{,}0x10^{-5}$-$1{,}0x10^{-4}$, co oznacza ryzyko na poziomie prawdopodobnym.

Wartości sumaryczne parametru HI obliczone dla 3 z 4 lokalizacji pomiarowych znajdowały się powyżej wartości 1, która stanowi wartość graniczną (jej przekroczenie świadczy o występowaniu ryzyka związanego z obecnością związków chemicznych w powietrzu atmosferycznym). Jedyną lokalizacją w której HI<1 był obszar reaktorów biologicznych. Wartości sumaryczne parametrów CR oraz HI zestawiono z wartościami stężeń zapachowych. Na podstawie obliczonych współczynników korelacji tych zmiennych wykazano, iż stężenie zapachowe na poziomie ok. 10 ou/m^3 odpowiada parametrowi CR na poziomie 1,0x10^{-5} (R^2=0,79), natomiast stężenie zapachowe < 15ou/m^3 odpowiada z wartości HI>1 (R^2=0,91). Uzyskane w ten sposób dane dają podstawę do możliwości wykorzystania metod olfaktometrycznych jako narzędzi do oceny ryzyka zachorowania w związku z obecnością w powietrzu związków zapachowych wykazujących właściwości chorobotwórcze. Podejście takie mogłoby stanowić nowe rozwiązanie, które oczywiście wymagałoby prowadzenia dalszych badań z wykorzystaniem zarówno technik instrumentalnych jak i sensorycznych.

Wyniki przeprowadzonych badań zostały przedstawione w pracy pt. *Evaluation of Health Hazard Due to Emission of Volatile Organic Compounds from Various Processing Units of Wastewater Treatment Plant*, opublikowanej w czasopiśmie *International Journal of Environmental Research and Public Health,* stanowiącej załącznik nr 4 do niniejszej rozprawy doktorskiej.

5.5 Realizacja celu badawczego nr 5

Osady ściekowe stanowią źródło emisji wielu szkodliwych związków chemicznych w tym związków uciążliwych zapachowo. Doniesienia literaturowe wskazują, iż największy wpływ na poziom nieprzyjemnego zapachu związanego z przetwarzaniem osadów ściekowych stanowią lotne związki siarkoorganiczne, które charakteryzują się bardzo niskimi wartościami progów wyczuwalności zapachowej. W związku z tym znaczna ilość prac doświadczalnych dotyczy wyłącznie tej grupy związków. Warto jednak zwrócić uwagę, iż wiele odorantów, występując na niskim poziomach stężeń i charakteryzując się wysokimi wartościami progów wyczuwalności zapachowej, może w istotny sposób zmieniać charakter odczuwanego zapachu. Zasadne wydaje się więc prowadzenie badań ukierunkowanych również na inne grupy związków, mogących potencjalnie wpływać na poziom odczuwanego zapachu związanego z operacjami przetwarzania osadów ściekowych.

Jedną z grup związków stosunkowo słabo opisaną w literaturze są lotne związki aromatyczne, głównie benzen, toluen, ksyleny oraz etylobenzen. Są to związki bardzo często identyfikowane w pracach badawczych dotyczących składu chemicznego osadów ściekowych. Większość procedur badawczych wykorzystywanych do oznaczania tych związków wykorzystuje etap przygotowania próbki z zastosowaniem stałego sorbentu (głównie technika mikroekstrakcji do fazy stacjonarnej lub sorpcję z zastosowaniem rurek z wypełnieniem w postaci stałego sorbentu). Rozwiązania te umożliwiają wzbogacenie analitów obecnych w próbkach na stosunkowo niskich poziomach stężeń. Problemem w niektórych przypadkach może być jednak odpowiedni dobór sorbentu, wykazującego wysokie powinowactwo do oznaczanych związków.

W trakcie przeprowadzonych badań wykorzystano technikę analizy fazy nadpowierzchniowej w połączeniu z techniką chromatografii gazowej sprzężonej z tandemową spektrometrią mas w celu opracowania procedury oznaczania 7 związków zapachowych z grupy lotnych związków aromatycznych (benzen, toluen, p-ksylen, etylobenzen, chlorobenzen, p-cresol oraz skatol). Możliwość stosowania niniejszej metody została zweryfikowana na podstawie oznaczeń tych związków w próbkach osadów ściekowych pobranych z trzech oczyszczalni ścieków z różnych etapów ich przetwarzania. Na podstawie uzyskanych wyników oraz informacji literaturowych dotyczących przemian jakim mogą ulegać oznaczane związki, podjęto próbę wyjaśnienia zaobserwowanych różnic w poziomach stężeń, głównie toluenu, p-krezolu oraz skatolu. W dyskusji do przedstawionych wyników stwierdzono również, iż wymienione powyżej związki mogą w istotny sposób wpływać na poziom nieprzyjemnego zapachu związanego z przetwarzaniem osadów ściekowych, gdyż ich wartości liczbowe progów wyczuwalności zapachowej są bardzo niskie.

Wyniki przeprowadzonych badań zostały przedstawione w pracy pt. *Differences between selected volatile aromatic compound concentrations in sludge samples in various steps of wastewater treatment plant operations*, znajdującej się obecnie w recenzji w czasopiśmie *Journal of Environmental Management*, stanowiącej załącznik nr 5 do niniejszej rozprawy doktorskiej.

5.6. Realizacja celu badawczego nr 6

Osady ściekowe, powstające w trakcie oczyszczania ścieków doprowadzanych do oczyszczalni stanowią jeden z głównych odpadów stałych, którego zagospodarowanie stanowi poważny problem. W 2016 roku wprowadzono w życie zakaz składowania osadów ściekowych na terenach składowisk odpadów. W związku z tym znacząco wzrosło zainteresowanie innymi – bardziej pro-ekologicznymi metodami ich zagospodarowania, głównie w rolnictwie oraz budownictwie. Jedną z najważniejszych operacji jednostkowych mających na celu ograniczenie procesu zagniwania osadów jest ich stabilizacja, prowadzona na drodze chemicznej, biologicznej lub termicznej. Jedną z najczęściej stosowanych metod biologicznej stabilizacji osadów jest proces fermentacji metanowej, prowadzony z jednoczesnym odzyskiem biogazu. Rozwiązanie to jest korzystne zarówno ze względu na wysoką skuteczność unieszkodliwiania osadów jak i możliwość odzysku energii w formie odnawialnej. Niemniej jednak osady po procesie fermentacji metanowej nadal mogą stanowić źródło wielu szkodliwych związków chemicznych, w tym związków potencjalnie uciążliwych zapachowo. Dlatego też ważne jest wykorzystanie dostępnych narzędzi matematycznych oraz wyników badań dotyczących składu chemicznego osadów ściekowych przed i po fermentacji, w celu opracowania rozwiązań umożliwiających przewidywanie właściwości zapachowych przefermentowanych osadów ściekowych.

W trakcie przeprowadzonych badań wykorzystano opracowaną wcześniej procedurę oznaczania lotnych związków aromatycznych techniką HS-GC-MS/MS w celu określenia poziomu stężeń 3 związków zapachowych należących do tej grupy związków (toluen, p-krezol oraz skatol) obecnych w próbkach osadów ściekowych zarówno przed oraz po procesie fermentacji metanowej. Próbki osadów ściekowych pobrano z dwóch oczyszczalni ścieków znajdujących się w woj. pomorskim. W ramach zaplanowanych badań przeprowadzono również analizy sensoryczne, w celu wyznaczenia intensywności zapachowej oraz jakości hedonicznej dla próbek przed oraz po fermentacji. Wykorzystując uzyskane wyniki oznaczeń chromatograficznych (stężenia toluenu, p-krezolu oraz skatolu), wyniki oznaczeń sensorycznych oraz dane dotyczące głównych parametrów procesu fermentacji metanowej, tj. zasadowość, pH oraz zawartość lotnych kwasów tłuszczowych, podjęto próbę oceny predykcji właściwości zapachowych próbek osadów ściekowych z użyciem sztucznych sieci neuronowych oraz drzew decyzyjnych. Wykazano, iż zastosowanie sztucznych sieci neuronowych o strukturze 8-4-2-1 umożliwia przewidywanie wartości intensywności zapachowej i jakości hedonicznej próbek osadów ściekowych na poziomie 25%. Zastosowanie drzewa decyzyjnego umożliwiło z kolei wskazanie właściwości sensorycznych, jakimi powinien charakteryzować się wsad fermentacyjny, aby ograniczyć uciążliwość zapachową osadów uzyskanych po procesie fermentacji. Przedstawione badania przeprowadzono w oparciu o stosunkowo niewielki zbiór danych – z tego względu wskazane wydaje się prowadzenie dalszych badań, umożliwiających wskazanie rozwiązań metodycznych, umożliwiających szybka kontrolę procesową procesu fermentacji metanowej, z uwzględnieniem zapachowego oddziaływania osadów ściekowych.

Wyniki przeprowadzonych badań zostały przedstawione w pracy pt. *The use of artificial neural networks and decision trees to predict the degree of odor nuisance of post-digestion sludge in the sewage treatment plant process*, znajdujące się obecnie w recenzji w czasopiśmie *Sustainability*, stanowiącej załącznik nr 6 do niniejszej rozprawy doktorskiej.

6. Wnioski końcowe

W trakcie realizacji poszczególnych zadań wynikających z zaplanowanego planu badawczego niniejszej rozprawy doktorskiej, podjęto próbę scharakteryzowania zapachowego oddziaływania lotnych związków organicznych, ze szczególnym uwzględnieniem związków zapachowych obecnych w próbkach osadów ściekowych. Dzięki zastosowaniu zaawansowanych rozwiązań instrumentalnych (techniki chromatograficzne oraz spektrometria mas) oraz sensorycznych (olfaktometria terenowa) możliwe było opisanie składu chemicznego próbek osadów ściekowych oraz próbek powietrza atmosferycznego, zawierającego w swoim składzie związki, których potencjalnym źródłem są osady ściekowe. Głównymi wnioskami z przeprowadzonych badań, stanowiącymi niewątpliwie element nowości naukowej są:

- kompleksowe wykorzystanie technik instrumentalnych i sensorycznych do oceny zapachowego oddziaływania osadów ściekowych;
- wykazanie możliwości stosowania w warunkach laboratoryjnych dynamicznej komory przepływowej w połączeniu ze spektrometrem mas z jonizacją poprzez reakcję przeniesienia protonu do określania poziomu emisji związków zapachowych uwalnianych z próbek osadów ściekowych (takie rozwiązanie nie było w tym zakresie jak dotąd stosowane);
- wykazanie korelacji pomiędzy stężeniem zapachowym próbek powietrza atmosferycznego pobranych z oczyszczalni ścieków a wystąpieniem zwiększonego ryzyka zachorowań w wyniku przedostawania się do organizmu związków zapachowych;
- opracowanie i przeprowadzenie walidacji procedury, umożliwiającej oznaczanie lotnych związków aromatycznych obecnych w próbkach osadów ściekowych z zastosowaniem techniki analizy frakcji nadpowierzchniowej w połączeniu z techniką chromatografii gazowej sprzężonej z tandemową spektrometrią mas;
- zaproponowanie wykorzystania sieci neuronowych oraz drzew decyzyjnych do przewidywania właściwości zapachowych osadów ściekowych poddawanych procesowi fermentacji beztlenowej.

W niniejszej pracy wykazano, iż wyniki badań dotyczących potencjalnych źródeł emisji związków zapachowych, uzyskiwane z wykorzystaniem zarówno technik instrumentalnych jak i sensorycznych mogą być ze sobą spójne i umożliwiać bardziej kompleksowy opis zjawisk związanych z powstawaniem substancji zapachowych i ich emisją do środowiska. Ważnym elementem niniejszej rozprawy było również wykazanie potencjału układu złożonego z dynamicznej komory przepływowej wraz ze spektrometrem mas z jonizacją poprzez reakcję przeniesienia protonu w badaniach nad poziomem emisji związków zapachowych uwalnianych z osadów ściekowych. W badaniach opisywanych do tej pory w literaturze, dynamiczna komora przepływowa była stosowana do określenia wielkości emisji w warunkach terenowych, np. w odniesieniu do poszczególnych elementów instalacji w oczyszczalniach ścieków. Rozwiązanie przedstawione w niniejszej pracy z powodzeniem może być stosowane również do monitorowania zmian w składzie związków chemicznych uwalnianych z różnych próbek stałych i ciekłych w trakcie przemian zachodzących w ustalonych warunkach.

Prowadzone badania przyczyniają się do poszerzenia obecnego stanu wiedzy i w przyszłości mogą umożliwić opracowanie kompleksowych rozwiązań metodycznych, umożliwiających w znaczący sposób ograniczenie negatywnego oddziaływania na środowisko obiektów gospodarki komunalnej, w tym oczyszczalni ścieków. Należy również pamiętać iż oddziaływanie człowieka na środowisko jest procesem naturalnym, jednakże należy być świadomym, iż konieczne jest podejmowanie wszelkich działań zmierzających ku temu, aby relacja ta była zachowana na bezpiecznym poziomie, gwarantującym zachowanie równowagi w środowisku.

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8. Dorobek naukowy

8.1. Publikacje naukowe

Podstawę niniejszej rozprawy doktorskiej stanowi cykl 6 prac oryginalnych opublikowanych w czasopismach znajdujących się w bazie Journal Citation Reports (JCR) o sumarycznym współczynniku oddziaływania (ang. Impact factor) IF=8,168. We wszystkich niżej wymienionych pracach jestem pierwszym autorem a w pięciu z nich również autorem korespondencyjnym.

[1] **Byliński H.**✉, Kolasińska P., Dymerski T., Gębicki J., Namieśnik J., Determination of odour concentration by TD-GCxGC-TOF-MS and field olfactometry techniques, Monatsch. Chem. 148 (9), 1651 (2017), (Q3, IF=1,285, MNiSW=25 pkt.);

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8.2. Rozdziały w monografiach książkowych

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8.3. Wystąpienia konferencyjne

Ustne wystąpienia konferencyjne:

- **Byliński H.**, Lewkowska P., Dymerski T., Gębicki J., Namieśnik J., Monitoring odorów na terenach przyległych do Rafinerii Grupy Lotos S.A. w Gdańsku z zastosowaniem techniki chromatografii gazowej i analizy sensorycznej; Pierwsza Międzynarodowa Konferencja Odorowa – Uciążliwość Zapachowa, Ocena, Pomiary i Kontrola, Gdańsk, 19-20.04.2016 r.
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8.4. Pozostałe osiągnięcia naukowe

- beneficjent stypendium z dotacji projakościowej w roku akademickim: 2016/2017, 2017/2018;

- beneficjent stypendium zadaniowego w ramach programu „Zintegrowany Program Rozwoju Politechniki Gdańskiej (ZIP)" w roku akademickim 2018/2019;
- recenzje wykonane na rzecz czasopism wyróżnionych w JCR

Czasopismo	**Liczba wykonanych recenzji**
Waste Management	1
Microchemical Journal	2

8.5. Działalność na rzecz Wydziału Chemicznego

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8.6. Wskaźniki naukometryczne

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9. Załączniki

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ORIGINAL PAPER

Determination of odour concentration by TD-GC×GC–TOF-MS and field olfactometry techniques

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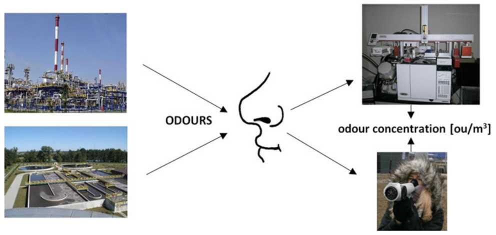
Abstract Field olfactometry is one of the sensory techniques used to determine odour concentration, in atmospheric air, directly in emission sources. A two-dimensional gas chromatography with time of flight mass spectrometer (GC×GC–TOF-MS) allows performing the chemical characterization of various groups of chemical compounds, even in complex mixtures. Application of these techniques enabled determination of odour concentration level in atmospheric air in a vicinity of the oil refinery and the neighbouring wastewater treatment plant. The atmospheric air samples were analysed during a time period extending from February to June 2016. Based on the GC×GC–TOF-MS analysis and odour threshold values, the theoretical odour concentrations were calculated and compared with the odour concentrations determined by field olfactometry technique. The investigations revealed that higher values of odour concentration were obtained with the field olfactometry technique where odour analysis was based on holistic measurement. It was observed that the measurement site or meteorological conditions had significant influence on odour concentration level. The paper also discusses the fundamental analytical instruments utilized in the analysis of odorous compounds and their mixtures.

Graphical abstract



Keywords Gas chromatography · Odorous substances · Mass spectroscopy · Field olfactometry · Wastewater treatment plant · Oil refinery

Introduction

All forms of human activity, including urbanization of the areas located close to residential buildings, have significant impact on the air quality. Increasing amount of pollutants originate from municipal facilities such as landfills, recycling factories or wastewater treatment plants. Industrial plants including oil refineries, manufactories, breweries, distilleries and others also have significant impact on the introduction of chemical compounds from various groups to the atmosphere [1–4]. Air pollutants can have adverse effect on living organisms and abiotic part of the environment. Some of these can have carcinogenic properties, so they can be very dangerous to human life, especially at high concentrations. Among air pollutants, particular attention should be directed to all substances, which can be responsible for unpleasant aroma in air—odours [5–8]. Olfactory properties are exhibited by numerous chemical

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compounds, mainly volatile organic compounds, organic and inorganic nitrogen derivatives (ammonia or amines), inorganic sulfur compounds (hydrogen sulphide, methyl and dimethyl sulphide, dimethyl disulphide), aldehydes, ketones, esters, carboxylic acids, aliphatic and aromatic hydrocarbons, fatty acids, terpenes or chlorinated hydrocarbons [9–13]. Some of these compounds have very low odour threshold and, despite low concentration in atmospheric air, they can have significant impact on odour nuisance level in some areas.

To determine the chemical compounds present in various samples including atmospheric air, gas chromatography coupled with mass spectrometry detector (GC–MS) is often used [14–16]. This technique allows identification and quantification of the components in the odour mixtures. For complex samples, successful results can be obtained using two-dimensional gas chromatography (GC×GC). In this technique, two capillary columns with various stationary phases are connected. Usually, the first column is longer and less polar than the second one. GC×GC–TOF-MS technique has been successfully applied in various areas, including food analysis [17], environmental studies [18], petrochemicals analysis [19], and forensic analysis [20].

The olfactometry techniques are widely used to assess the sensory properties of many chemical compounds. During each analysis, the sense of smell is used as a measurement device. Among the sensory techniques used to determine the odour concentration, dynamic olfactometry enjoys an increasing popularity [21]. This method was described in the following standard: EN 13725 (2003) Air quality—determination of odour concentration by dynamic olfactometry, translated into Polish in 2007 [22]. To determine the odour concentration directly in emission sources, the field olfactometry technique is used [23]. Due to the possibility of determining small and quickly changing values of odour concentration, the field olfactometry (FO) technique is more and more frequently used to evaluate and monitor olfactory sensation, which can originate from various forms of human activities. The results from sensory evaluation allow identification of sources of odorants and estimation of the total odour emission in a particular measurement point at a particular period of time [24, 25]. One of the disadvantages of this technique is the necessity of an experienced panellists' team, whose sensory sensitivity must be verified regularly. During long periods of time, the sensory sensitivity can deteriorate due to different factors, mainly olfactory fatigue. Field olfactometry technique finds increasing application in the evaluation of odour impact of different plants as the potential sources of odorous compound emission, for example, pig farms [26], mink farms [27], and sewage treatment plants [28–31].

Literature provides some papers concerning the comparison of different analytical techniques constituting the potential tools for odour quality evaluation. Capelli et al. [32] compared three instrumental techniques: GC–MS, dynamic olfactometry, and electronic nose technique as the potential tools allowing evaluation of the odour nuisance due to operation of a municipal landfill. Application of the GC–MS allowed determination and comparison of theoretical odour concentration, with the odour concentration determined by the dynamic olfactometry technique. As a result, there was a lack of correlation between the obtained results. Such situation was explained by the impossibility to measure all phenomena occurring in the odour mixture (odour synergism, odour attenuation) in case of determination of the theoretical odour concentration. The investigations carried out with the electronic nose instrument proved the ability of this technique to monitor changes of atmospheric air composition, for instance due to failure of industrial devices and installations. The authors emphasize that despite the lack of correlation between the results obtained with all three presented measurement techniques, each of them exhibits significant added value to the odour measurement problem as odour perception is a complex phenomenon. Another paper [8] presents the potentialities of several instrumental solutions aimed at characterization of the most important odorous substances present in atmospheric air, the emission of which is connected with the operation of a landfill. Among the presented techniques, there were gas chromatography–flame ionization detector and pulsed flame photometric detector (GC–FID/PFPD) as well as high-performance liquid chromatography (HPLC). The theoretical values of odour concentration were determined based on the concentration of particular chemical compounds and odour threshold values. In that paper, the authors proved the possibility of using this information to estimate the relative odour strength originating from the compounds present in atmospheric air.

Hansen et al. [33] utilized proton transfer reaction-mass spectrometry (PTR-MS) and dynamic olfactometry techniques to evaluate the effectiveness of a technology aimed at limitation of emission of odorous compounds generated by a pig farm. The investigations were carried out directly at the emission source (a mobile laboratory equipped with an olfactometer and spectrometer) as well as in the laboratory (air samples were collected into bags and olfactometric evaluation involved dynamic olfactometry technique). Comparison of the obtained results revealed substantial discrepancy between the odour concentrations obtained via dynamic olfactometry at the source as well as in the laboratory and the theoretical odour concentrations (named by the authors as "odour activity values"). A need for further investigation aimed at limitation of odour changes connected with air sampling into the bags was emphasized.

The purpose of this paper was to investigate the capability of two-dimensional gas chromatography coupled with time of flight mass spectrometer and field olfactometry techniques for characterization of the odour properties of atmospheric air in the part of Gdańsk City. In this area, a wastewater treatment plant and an oil refinery—one of the biggest industrial plants in the Pomeranian Voivodeship—are located. This research can show odour nuisance level over a period of 6 months and determine some factors, including atmospheric conditions, which can have significant impact on the odour nuisance. The paper contains a comparison of the theoretical odour concentrations obtained with the GC×GC technique with the odour concentrations acquired using field olfactometry. The reasons for the observed differences were discussed.

Results and discussion

Sensory analysis

Field olfactometry technique makes it possible to read out the values of “dilution to threshold ratio” (*D*/*T*). This parameter shows the ratio of the air stream that passed through the carbon filter (V_{clean}) to the stream of odorous air (V_{crude}). Based on the *D*/*T* values and Eq. (1), two values of dilution ratios were calculated: Z_{YES}—dilution ratio corresponding to the first setting of *D*/*T*, when the odour became perceptible; Z_{NO}—dilution ratio corresponding to the setting of *D*/*T* preceding the setting in Z_{YES}.

$$Z = \frac{V_{\mathrm{clean}} + V_{\mathrm{crude}}}{V_{\mathrm{crude}}} = \frac{V_{\mathrm{clean}}}{V_{\mathrm{crude}}} + 1 = \frac{D}{T} + 1. \quad (1)$$

Table 1 Average concentrations of odours at each measurement point during 5-month period of time/ou/m^3

Measurement point	Month				
	II	III	IV	V	VI
P1	1.7	1.7	1.7	1.7	1.7
P2	3.1	3.5	4.5	5.1	6.2
P3	3.7	4.4	3.9	6.9	7.4
P4	1.7	1.7	1.7	1.7	1.7
P5	1.7	1.7	1.7	1.7	1.7

To estimate the odour concentration, individual odour threshold estimate (Z_{ITE}) was calculated as a geometric mean of the Z_{YES} and Z_{NO} values (Eq. (2)):

$$Z_{\mathrm{ITE}} = \sqrt{Z_{\mathrm{YES}} \times Z_{\mathrm{NO}}}. \quad (2)$$

Odour concentrations were calculated as a geometric mean of Z_{ITE} from each measurement point.

In Table 1, the concentrations of odours at each measurement point (P1–P5) were presented. It can be observed that at two points—P2 and P3—the values of this parameter are significantly higher than in the remaining three measurement points. P2 and P3 points are located within the closest distance from two potential emitters of air pollution including odorous compounds—the wastewater treatment plant and the oil refinery. It could be one of the main reasons of higher values of odour concentration at these two points. Atmospheric conditions (air temperature, humidity, wind speed and direction) could also have a significant impact on the obtained results. Meteorological conditions during sampling are presented in Table 2. Based on the meteorological parameters shown in Table 2, it can be easily noticed that north and north-west winds were predominant during the time of olfactometric measurements. These winds could have moved air masses towards the points P2 and P3 located south with respect to the oil refinery, thus contributing to elevated odour concentrations at these measurement points.

The odour concentrations from P2 and P3 points were collected and compared in each month of sampling with the air temperature and humidity (Fig. 1). It can be observed that an increase in odour concentration occurs with an increase in air temperature and a decrease in air humidity. These parameters are very important from the viewpoint of determination of odour concentration in various times. In February–March–April, the minimum odour concentration was very similar, while in May and June these values were

Table 2 Meteorological conditions during sampling in each month

Month	Air temperature/°C			Air humidity/%			Wind speed/m/s			Wind direction
	Min.	Max.	Abr.	Min.	Max.	Abr.	Min.	Max.	Abr.	
II	−3.3	9.1	2.9	64.6	96.4	80.5	2.3	14.5	8.4	NW
III	−1.0	15.8	7.4	57.0	96.5	76.8	3.5	17.3	10.4	NW/N
IV	0.8	20.7	10.8	46.7	96.4	71.6	4.9	17.4	1.,2	NW
V	6.1	28.3	17.2	38.2	97.0	67.6	3.7	12.2	8.0	N/SW
VI	7.7	32.3	20.0	27.7	97.4	62.6	3.1	12.6	7.9	N/NW

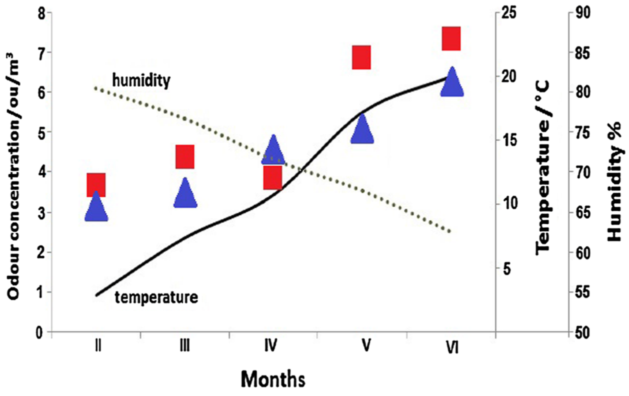

Fig. 1 Comparison of odour concentration with respect to air temperature and humidity (*blue point* average concentration from P2, *red point* average concentration from P3)

significantly different (Fig. 1). The maximum odour concentration was growing during the February–May period; in May and June these values were very similar.

Chromatography analysis

Application of two-dimensional gas chromatography enabled identification of the main chemical compounds present in atmospheric air at the areas adjacent to the potential sources of these pollutants. Table 3 presents the main chemical compounds identified at one of the measurement points located in the vicinity of the oil refinery and the wastewater treatment plant. The identified chemical compounds were the most abundant ones on chromatograms. Moreover, the criteria of $S/N > 10$ was fulfilled in each case, which means that the substance appears above the limit of quantification (LOQ).

Figure 2 illustrates an exemplary 2-D chromatogram of the main compounds identified in point P3 in June. It can be observed that chemical substances belonging to different chemical classes have similar physicochemical properties, namely volatility, which can cause a co-elution in the first retention time. Therefore, application of the GC × GC system is important to separate chemical compounds with respect to two independent retention mechanisms based on volatility and polarity. In this case, it is possible to obtain a full separation. Some of these chemical compounds are responsible for malodour. Different odour properties such as odour intensity, hedonic quality, type of smell, concentration of each compound in the air and exposition time have significant impact on the level of odour nuisance in the area. Among the identified chemical compounds, many have characteristic odour and in many cases their smell is different despite being members of the same group of chemical compounds.

Dominant groups of chemical compounds identified in atmospheric air in the vicinity of the oil refinery and the neighbouring wastewater treatment plant are aliphatic hydrocarbons, aromatic hydrocarbons, aldehydes, ketones, terpenes and esters. Their presence is connected with the operation profile of the plants located in the neighbourhood of the investigated area and with the air masses transported from other parts of Gdańsk City.

Determination of theoretical odour concentration and comparison with odour concentration

Theoretical odour concentration ($C_{\mathrm{od\ OT}}$) was calculated as a sum of chemical concentrations of all chemical compounds identified in one location (C_{i}) and their odour threshold (OT_{i}) ratio (Eq. (3)); N is the number of compounds.

$$C_{\mathrm{odOT}} = \sum_{i=1}^{N} \frac{c_i}{OT_i}. \tag{3}$$

Table 4 shows the calculation of theoretical odour concentration at point P3 in June. A comparison of the theoretical odour concentration ($C_{\mathrm{od\ OT}}$) and the odour concentration determined by field olfactometry technique ($C_{\mathrm{od\ FO}}$) in each month is presented in Table 5.

A difference observed between the odour concentrations determined with GC×GC and field olfactometry can stem from several reasons. Chromatographic investigation provides separation of odorous mixture into particular components and thus yields qualitative and quantitative information about them. It is impossible to predict if these components exhibit odour-related mutual interaction, causing for example synergism (amplification of odour) or neutralization (attenuation of odour). In case of the olfactometric studies, where holistic measurement is performed, such effects can be observed and measured. The next factor, which can determine the obtained results, is the lack of unequivocal and universal odour threshold values. Literature provides several values of this parameter for particular compounds [13, 34–40], which result in underestimation or overestimation of the theoretical concentration. Another factor that determines the observed concentration difference is the limited number of chemical compounds identified and measured using GC×GC. Despite this fact, a relatively good correlation between the obtained results can be noticed that can be an evidence of a certain complementary character of the measurement techniques applied.

Conclusion

Using two-dimensional gas chromatography technique allows quantitative and qualitative analysis of the main pollution present in atmospheric air at the areas adjacent to

Table 3 Main chemical compounds identified at measurement point P3 in June

Name	First retention time/seconds	Second retention time/minutes	Similarity	*S*/*N*	Unit mass
Ethanol	320	2.37	952	18,043	27
2-Methylbutane	330	1.93	919	16,553	57
Pentane	340	1.94	891	8209.5	57
2,2-Dimethylbutane	355	1.94	921	16,415	57
Acetaldehyde	380	2.16	820	178.66	42
Hexane	410	1.98	947	17,862	86
2-Butenal	440	3.13	885	269.94	70
Benzene	465	2.17	964	60,419	78
Pentanal	500	2.27	939	7966.5	58
3-Ethyl-2,2-dimethylpentane	510	1.99	858	23,634	57
Toluene	635	2.46	936	1688.3	91
Ethyl butyrate	685	2.30	939	4338.0	71
Propyl propanoate	700	2.48	898	236.76	57
m-Xylene	830	2.53	713	31.124	91
Ethylbenzene	845	2.32	965	45,184	51
3-Ethylheptane	870	2.06	895	2850.5	57
o-Xylene	895	2.39	968	20,445	91
Propyl butyrate	895	2.30	851	144.69	88
Benzaldehyde	1015	3.52	971	13,159	106
Sabinene	1015	2.07	934	23,114	136
Pinene	1050	2.09	936	12,681	77
Hexadecane	1105	2.47	798	135.92	57
D-Limonene	1125	2.13	932	92,392	136
Terpinene	1155	2.18	884	11,991	93
Methyl heptanoate	1190	2.57	907	990.03	74
2-Ethyl-1-hexanol	1215	2.52	939	3844.1	112
5-Ethyl-2-methylheptane	1230	2.07	900	4667.6	71
Camphene	1235	2.15	954	13,609	121
Dodecane	1330	2.06	902	2112.8	71
Nonanal	1375	2.48	924	987.47	57
2-Ethylhexanoic acid	1430	4.40	886	1645.5	73
Tetradecane	1665	2.08	859	575.51	57
Hexadecanal	2020	2.42	890	107.21	57
Pentadecane	2135	2.06	874	304.14	57
1-Heptadecene	2595	2.10	829	23.197	31

the potential odour emitters, such as the wastewater treatment plant and the oil refinery located in the south-east part of Gdańsk City. Based on this analysis, it is possible to calculate the theoretical odour concentration and to compare it with the odour concentration determined by field olfactometry technique. The determined theoretical odour concentrations varied from 1.7 to 4.6 ou/m^3 depending on the measurement site (P2 and P3) and season of the year. In the case of theoretical determination of odour concentration based on the concentration of particular substances, it is not possible to take into account all phenomena connected with mutual odour amplification of particular components of an odour mixture. Both odour amplification—synergism—and odour attenuation can significantly change the strength of the odour sensed by humans. During the investigation described in the paper, it was impossible to identify all chemical compounds present in atmospheric air, which could have had an influence on the odour perception level. The aforementioned problems do not exist when the odour concentration is determined with field olfactometry technique. Olfactometric examination is a holistic approach; so it allows measurement of the entire odour mixture. The odour concentrations obtained with field olfactometry varied from 1.7 to 7.4 ou/m^3 depending

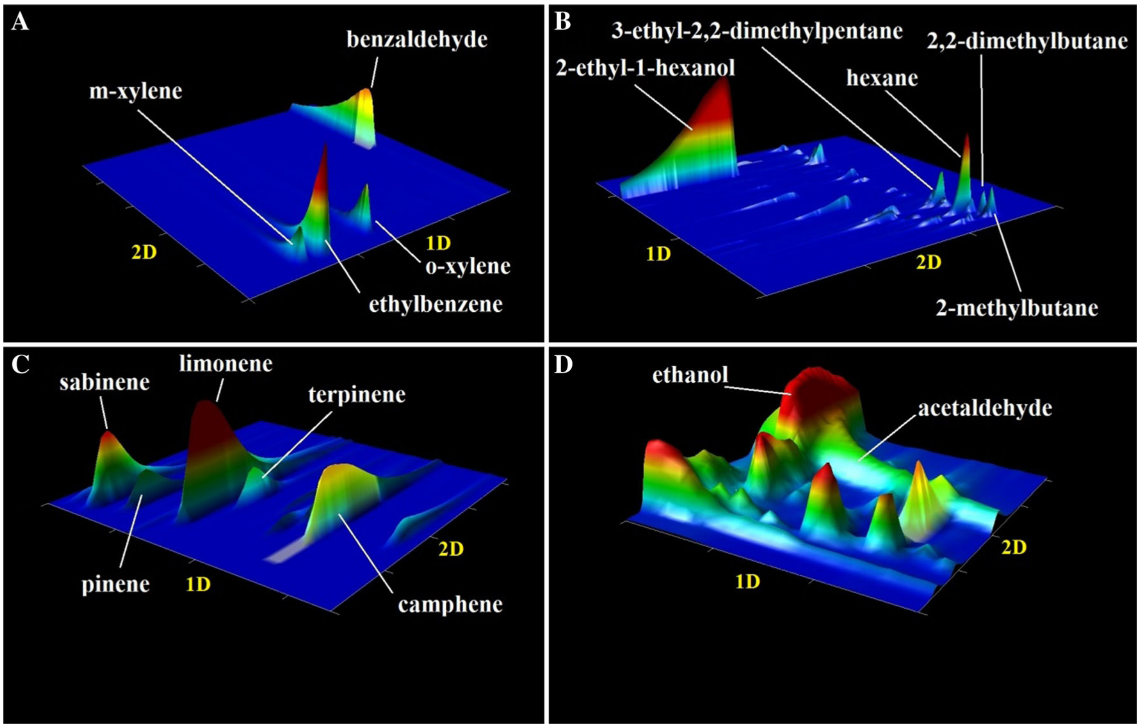

Fig. 2 Chromatograms 2-D of the main compounds identified in the measuring point P3 in June

on the measurement site and season of the year. An increase in temperature is accompanied by intensification of decay processes occurring in wastewater treatment plants, which generate much higher amount of volatile compounds, including malodorous ones. In the case of oil refineries, the following phenomena take place: sweating of tanks at high temperature, leaking valves, leakages, and non-organized emission. These factors can contribute to enhanced emission of the odorous compounds.

The main chemical compounds identified during the investigations performed include aromatic and aliphatic hydrocarbons, aldehydes, ketones, terpenes, and esters. The compounds were present at the level of 1.4–8.7 ppb v/v depending on the site and the time of the measurement.

Weather conditions (wind speed, air temperature and humidity) were also monitored to show some correlation. Based on this research, an increase in odour concentration occurs with an increase in air temperature and a decrease in air humidity during the entire time period (5 months). High temperature increases the odour intensity and consequently the strength of the perceived odour. A higher content of water in the air can absorb some volatile compounds and the overall unpleasant odour is relatively smaller than in reality. Potentialities and limitations of particular techniques suggest that the most convenient solution is simultaneous application of a few methods, supplementary in character. Such approach allows complete illustration of the odour nuisance phenomenon, beginning with odour origination in different industrial or municipal facilities, through emission and immission processes, finishing with evaluation of exposure hazard of individuals or communities to unpleasant odour over a particular area.

Experimental

Sampling

The atmospheric air samples were collected during the 5-month period of time between February and June 2016 in the south-east part of Gdansk City. Every month, three measurement series were performed. The operation of the manufacturing plant (one of the biggest industrial plants in northern Poland) and the wastewater treatment plant located in this area can be connected with large emission of pollutants into the air.

The oil refinery located at this area has its own air monitoring stations in some of these points, where the concentration of the selected pollutants (methane, BTEX compounds, summary concentration of hydrocarbons and non-methane hydrocarbons) is measured. This area was selected for investigation due to close vicinity of two objects constituting a potential source of air pollution with odorous compounds—wastewater treatment plant and oil refinery. Localization of the measurement points was chosen in a way, which allowed revealing potential

Table 4 Calculation of theoretical odour concentration at point P3 in June

Chemical compound	Chemical concentration (C_i) ± standard deviation (SD)/ppb	Odour threshold (OT_i)/ppb [13, 34–36]	C_i/OT_i
Benzene	4.9 ± 0.5	2700	0.0016 ÷ 0.0020
Toluene	4.3 ± 0.4	330	0.0118 ÷ 0.0142
Ethylbenzene	5.7 ± 0.6	170	0.0300 ÷ 0.0370
m-Xylene	3.5 ± 0.4	41	0.0756 ÷ 0.0951
o-Xylene	6.7 ± 0.6	58	0.1051 ÷ 0.1258
p-Xylene	2.2 ± 0.2	380	0.0052 ÷ 0.0063
Limonene	6.6 ± 0.7	38	0.1552 ÷ 0.1921
α-Pinene	5.2 ± 0.6	18	0.2555 ÷ 0.3222
Pentane	4.3 ± 0.4	1400	0.0027 ÷ 0.0034
Hexane	8.2 ± 0.9	1500	0.0049 ÷ 0.0061
Heptane	3.6 ± 0.4	670	0.0048 ÷ 0.0060
Octane	4.9 ± 0.6	1700	0.0025 ÷ 0.0032
Nonane	6.1 ± 0.6	2200	0.0025 ÷ 0.0030
Decane	5.9 ± 0.7	620	0.0084 ÷ 0.106
Undecane	4.8 ± 0.5	870	0.0049 ÷ 0.0061
Dodecane	5.2 ± 0.5	110	0.0427 ÷ 0.0518
Acetaldehyde	4.4 ± 0.6	1.5	2.5333 ÷ 3.3333
Benzaldehyde	4.6 ± 0.6	42	0.0952 ÷ 0.1238
Sabinene	5.8 ± 0.7	75	0.0680 ÷ 0.0867
Phenol	5.1 ± 0.5	47	0.0978 ÷ 0.1191
Styrene	4.5 ± 0.5	47	0.0851 ÷ 0.1064
Biphenyl	6.1 ± 0.5	48	0.1167 ÷ 0.1375
1,3,4-Trimethylbenzene	4.4 ± 0.3	170	0.0241 ÷ 0.0276
1,3-Diethylbenzene	3.8 ± 0.5	70	0.0471 ÷ 0.614
1-Methylcyclohexane	4.8 ± 0.6	150	0.0280 ÷ 0.0360
2-Methylheptane	3.1 ± 0.5	110	0.0236 ÷ 0.0327
		Summary	3.8 ÷ 4.9

Table 5 Comparison of theoretical odour concentration ($C_{od\ OT}$) and odour concentration ($C_{od\ FO}$) for points P2 and P3

Location	II		III		IV		V		VI	
	$C_{od\ OT}$	$C_{od\ FO}$	$C_{od\ OT}$	$C_{od\ FO}$	$C_{od\ OT}$	$C_{od\ FO}$	$C_{od\ OT}$	$C_{od\ FO}$	$C_{od\ OT}$	$C_{od\ FO}$
P2	1.9	3.1	2.4	3.5	2.6	4.5	3.5	5.1	4.6	6.2
P3	2.1	3.7	1.7	4.4	1.9	3.9	4.3	6.9	4.4	7.4

differences in ambient air quality around these objects. The measurement points P2–P4 were localized in the neighbourhood of the oil refinery and the wastewater treatment plant, whereas the measurement points P1 and P5 were in the vicinity of the oil refinery (Fig. 3).

A device called gas sampling system (GSS, Gerstel, Germany) was used for sample collection. This device allows collection of chemical compounds on the solid sorbent poly(oxy-2,6-diphenyl-1,4-phenyl) into the special tubes by pumping atmospheric air through these tubes. Before sampling, each tube was subjected to thermal desorption (temperature 280 °C, time of desorption 180 min) to remove potential pollution from previous studies. Between desorption and sampling, the sampling and analysis tubes were stored in dedicated containers at 15 °C. The volumetric flow rate of air through the tubes was 75 cm^3/min and the sampling time equalled 30 min for each tube.

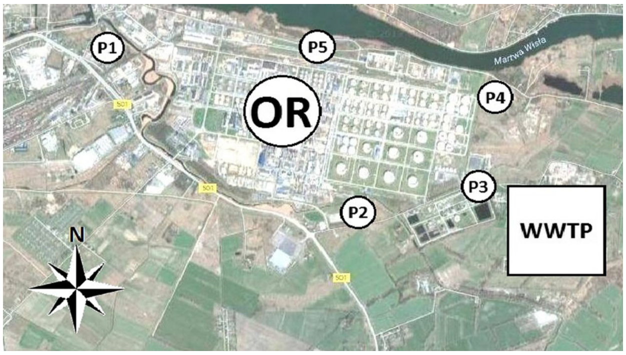

Fig. 3 Location of measurement points; *OR* oil refinery, *WWTP* wastewater treatment plant [41]

Instrumentation

To determine the chemical compounds present in atmospheric air over the investigated area, the air samples were analysed using a two-dimensional gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a cryogenic modulator and coupled with a time-of-flight mass spectrometer (LECO Corp., St. Joseph, MI, USA). The column set consisted of a 30 m × 0.25 mm 0.25 µm primary column (1D) with Equity 1 stationary phase (Sigma Aldrich, USA) and a 2.0 m × 0.10 mm × 0.10 µm secondary column (2D) with Sol Gel Wax stationary phase (SGE Analytical Science, Australia). Separation of sample components was performed using the following optimized temperature programme for the primary GC oven:

- initial temperature of 40 °C,
- constant temperature for 1 min,
- temperature ramped at 10 °C/min to 90 °C,
- temperature ramped at 3 °C/min to 240 °C,
- constant temperature for 5 min,

and for the secondary GC oven:

- initial temperature of 45 °C,
- constant temperature for 1 min,
- temperature ramped at 10 °C/min to 95 °C,
- temperature ramped at 3 °C/min to 245 °C,
- constant temperature for 5 min.

The total analysis time was 65 min. Helium was used as a carrier gas (at a constant flow rate of 1.0 cm^3/min). A modulation period of 5 s was employed with the cryogenic trap cooled to −196 °C using liquid nitrogen. The temperatures for the transfer line and the ion source were maintained at 250 °C. The detector voltage was set to 1600 V. Ions in the $m/z = 40$–500 range were analysed.

Sensory analysis

Sensory analysis was performed using a Nasal Ranger field olfactometer (St. Croix Sensory, USA). The operation principle of this device is based on mixing odorous air and the air passed through a dedicated carbon filter in various proportions and evaluation of sensory properties of these mixtures by panellists. Before measurement series, the panellists (four people) were trained with regard to sensory evaluation, and the sensitivity of their sense of smell was checked according to a standard procedure employed to determine an individual sensitivity level of the sense of smell, developed by St. Croix Sensory, Inc. (St. Croix Sensory 2006, Minnesota). During each measurement series (3 days in each month), they were asked to indicate at which step of air dilution by odourless air the odour became perceptible. In each measurement point, each panellist conducted three evaluations at 10-min intervals. The measurements in each location were taken by all four panellists at the same time. Olfactometric evaluation was carried out simultaneously with a collection of the air samples intended for the analysis using two-dimensional gas chromatography.

Data analysis

Data analysis was performed using the algorithm for peak deconvolution included in the Chroma TOF software (LECO Corp., USA, version 4.44). Tentative identification was accomplished through MS library search using the NIST 2011 and Willey 11 mass spectral library.

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ORIGINAL PAPER

Complementary use of GCxGC–TOF–MS and statistics for differentiation of variety in biosolid samples

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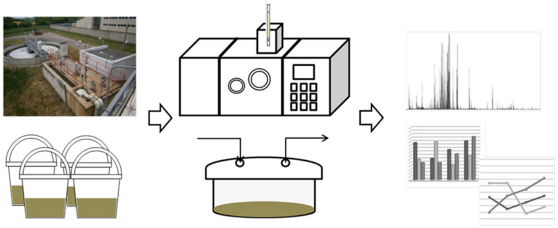
Abstract

Formation of biosolid cakes, which are one of the main wastes generated in wastewater treatment plants, is connected with emission of many hazardous chemical compounds, including odoriferous ones. To optimize particular processes of biosolid cake processing, it is necessary to assess chemical composition of the gas mixtures containing the compounds released from the cakes. The paper proposes application of two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GCxGC–TOF–MS) to identification of the compounds released from four main types of biosolid cakes and to quantitative determination of the markers characteristic for particular types of cake. Based on the analysis of variance, the following compounds, which could be potential markers of the investigated biosolid cakes, were selected: 1-propanol, 2-hexanone, toluene, *o*-xylene, *p*-xylene, and organosulfur compounds (methanethiol, ethanethiol, dimethyl sulfide, dimethyl disulfide, and diethyl disulfide). Theoretical odour concentrations of four investigated types of biosolid cakes were determined, based on measured concentrations and olfactory thresholds of the aforementioned compounds. The highest concentration was revealed for a primary cake (634 ou/m^3), whereas the lowest concentration was found for an excess cake (136 ou/m^3) (ou/m^3—odour unit per m^3; one odour unit is equivalent to collective odour threshold of odorants mixture present in 1 m^3). The proposed methodology allows preliminary evaluation of the odour nuisance markers connected with formation of the biosolid cakes, without a need for quantitative analysis of all determined compounds.

Graphical abstract



Keywords Gas chromatography · Mass spectroscopy · Odoriferous substances · Biosolid samples · Wastewater treatment plant

Introduction

Operation of wastewater treatment plants is accompanied by generation of biosolid cakes, which are the sources of numerous hazardous chemical compounds, including malodorous ones [1–3]. The substances released during processing of the biosolids are complex mixtures of volatile organic compounds, with a significant contribution of organosulfur compounds, aldehydes, ketones, esters, and

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alcohols [4, 5]. Their content is strongly dependent on size of the city agglomeration and industrialization of the regions, from which sewage is collected as well as on a treatment technology employed. Selection of the optimum technology of biosolid cake processing should take into account changes in concentration level of particular chemical compounds. It is a very difficult task in case of the waste, including biosolids, generated in the wastewater treatment plants; the reason is variety in chemical composition of the material supplied [6].

The main unit operations, such as biosolid stabilization, composting, dewatering, drying, or thermal processing, are carried out in the wastewater treatment plants to limit negative environmental impact [7]. Execution of these processes is indispensable for further processing of the biosolid cakes; however, it does not ensure total removal of all potentially hazardous chemical and odoriferous compounds [8]. The investigations on the determination of the compounds released from the biosolid cakes show that their variety significantly hinders identification of those, which have the most negative influence on the environment. It is also difficult to point these compounds, which have the biggest impact on nuisance that affects the employees of the wastewater treatment plants and the residents of the areas neighbouring such municipal objects. That is why, it is necessary to elaborate a methodology of determination of the compounds released from the biosolid cakes, based on the instrumental tools available. This procedure should also utilize statistical and chemometric methods available. Significant optimization possibilities are created by statistical tests, which make it possible to define mutual correlation between investigated samples, including analysis of variance [9–12].

One of the technical solutions enabling measurement of emission of volatile odoriferous compounds, released from solid or liquid specimens surfaces (including the biosolid cakes), is application of the enclosure chambers [13]. In 1986, the Unites States of America Environmental Protection Agency (US EPA) issued a document regulating emission measurements using a flux hood chamber [14]. Its operation consists in: isolation of the investigated surface, blowing with high purity gas, and then measurement of the analytes using selected instrumental solution [15]. Chromatographic techniques, mainly gas chromatography coupled with mass spectrometry, are the most frequently used for determination of chemical composition of odoriferous gas mixtures. Popularity of this solution stems from the possibility of measurement of the components present at trace concentration level in the samples of various origin and composition [16, 17]. In the case of separation of complex mixtures of chemical compounds, one-dimensional chromatographic analysis can be insufficient for the identification of a wide array of the substances present in the samples. An alternative solution is two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GCxGC–TOF–MS), which is characterized by better resolution than the GC–MS technique [18, 19]. It results from the fact that the components of investigated sample, which are present in a mobile phase, leave the first chromatographic column and then they are collected and fractionally dosed into the second column using a modulator (being central element of the GCxGC system). Both columns differ in polarity of the stationary phase, which allows an increase in selectivity [20, 21]. The GCxGC–MS technique provides the information about qualitative and quantitative composition of the investigated samples characterized by complex matrix composition [22]. Waste generated in the wastewater treatment plants, including the biosolid cakes, belongs to aforementioned type of the samples, and hence, selection of the GCxGC technique is fully justified.

The aim of performed investigation was an attempt to identify those chemical compounds released from four types of biosolid cakes, which could be their potential markers. Identification of the compounds enabling differentiation between particular types of biosolids was based on the results of qualitative analysis employing the GCxGC–TOF–MS technique and analysis of variance. Quantitative analysis of the compounds and their olfactory thresholds provided theoretical odour concentrations for four investigated types of biosolid cakes.

Results and discussion

VOCs identified

Using the GCxGC–TOF–MS system, it was possible to identify the volatile chemical compounds emitted from various biosolid samples produced in WWTPs. As an example, Table 1 lists the chemical compounds emitted from the primary sludge. It can be observed that dominant groups of volatile substances emitted from the biosolid samples are: aldehydes, ketones, sulfur compounds, and aromatic hydrocarbons. These groups of VOCs have previously been reported in the other studies [23–25]. However, in some cases, the chemical compounds belonging to different classes can have similar physicochemical properties and it causes a co-elution in the first retention time. As a result, it is not possible to separate all of the substances present in analysed samples. Application of two-dimensional gas chromatography system allows obtaining full separation of determined compounds. It is a consequence of using two independent separation mechanisms based on volatility and polarity.

Table 1 Chemical compounds emitted from primary sludge

1st RT/s	2nd RT/s	Name of compounds	Similarity[a]
270	1.46	2-Propenal	876
278	1.22	Methanethiol	881
286	2.19	Acetonitrile	966
286	1.74	Ethanol	939
290	1.38	2-Propanone	926
290	1.46	2-Propenal	875
290	1.32	Propanal	894
294	1.21	Ethanethiol	907
302	1.33	Dimethyl sulfide	919
310	2.31	1-Propanol	937
318	1.33	Diethyl disulfide	918
326	1.66	2-Butanone	946
330	1.55	Butanal	952
350	1.54	2-Ethylbutanal	970
370	1.66	Benzene	901
374	1.28	2-Hexanone	906
378	1.18	Pentanal	876
386	1.55	3-Ethyl-3-pentanol	939
446	2.16	Dimethyl disulfide	973
478	1.89	Toluene	933
478	2.98	Pyridine	968
506	2.00	2-Methyl-3-heptanol	876
510	2.02	Hexanal	897
566	2.26	Methyl ethyl disulfide	879
578	1.22	Butane	863
614	2.00	Ethylbenzene	940
626	2.04	1,4-Dimethylbenzene	960
650	2.20	2-Heptanone	972
658	2.15	Methyl propyl disulfide	916
666	2.16	Heptanal	902
666	2.20	1,2-Dimethylbenzene	895
694	1.26	Nonane	931
706	1.31	1-Decanol	854
750	1.24	Decane	878
754	1.42	α-Pinene	927
762	2.02	Benzaldehyde	966
766	1.91	2-Ethylhexanal	931
778	1.51	Camphene	874
794	3.65	Benzonitrile	937
822	1.28	3-Ethyloctane	885
826	2.24	2-Octanone	940
846	2.20	Octanal	943
858	1.19	Phenol	874
874	1.64	α-Phellandrene	870
894	2.39	1,3,5-Trimethylbenzene	934
918	1.68	Limonene	929
954	1.90	Acetophenone	937
970	1.72	α-Terpinene	910
978	2.09	1-Methyl-2-propylbenzene	963
1050	2.82	3-Pentanol	865
1234	3.88	Benzothiazole	897
1514	1.46	Acetic acid, decyl ester	921

[a] Similarity: average of similarity of the mass spectrum of identified compounds to the spectra of standard compounds in the NIST 2011 library

Percentage contributions of chemical classes in the tested biosolid samples are presented in Table 2. It can be observed that sulfur compounds are dominant group of the chemical compounds in primary and dewatered sludge (28 and 25%, respectively). In waste-activated sludge, aliphatic hydrocarbons, alcohols, and ketones are the most significant groups of chemical compounds. Dominant group of the chemical compounds in digested sludge is aliphatic hydrocarbons. Changes in the percentage contribution of chemical classes in various types of biosolids are strongly related to operation of WWTPs. During biological treatment, percentage contribution of sulfur compounds decreases, but sludge dewatering operation results in a significant increase in concentration of these compounds. Percentage contribution of aromatic hydrocarbons, which are one of the dominant groups of chemical compounds in the biosolid samples, is very similar for each type of sludge (from 12% in waste-activated sludge to 19% in dewatered sludge). Similarly, percentage contribution of alcohols does not change significantly during sludge treatment (from 16% in dewatered sludge to 21% in waste-activated sludge).

Estimation of key odoriferous compounds emitted from biosolid cakes

Table 3 presents surface area of the chromatographic peaks obtained for 20 chemical compounds, identified in volatile fraction of the investigated biosolid cakes, which have the biggest influence on the result of the performed statistical analysis. These compounds were divided into four chemical classes: alcohols, ketones, aromatic compounds, and organosulfur compounds, to find some dependences occurring within particular groups of the compounds. The statistical analysis revealed that each of the four types of biosolid cakes had different, statistically significant, composition of the volatile fraction. Significant differences

Table 2 Percentage contributions of chemical classes in the tested biosolid samples

Chemical classes	Primary sludge (%)	Waste-activated sludge (%)	Digested sludge (%)	Dewatered sludge (%)
Sulfur compounds	28	9	7	25
Aromatic hydrocarbons	16	12	14	19
Aldehydes	10	9	11	6
Ketones	9	20	11	9
Aliphatic hydrocarbons	9	20	25	16
Alcohols	19	21	18	16
Others	9	9	14	9

Table 3 Differentiation between main VOCs emitted from biosolid samples; mean values ($n = 3$) ± SD; different letters in the same line indicate significant differences among volatiles in each biosolid samples (Tukey's HSD test. $P < 0.05$)

Chemical compound	Chromatographic peak area/mean ± SD $(\times 10^{-3})$			
	PS[a]	WAS[a]	DGS[a]	DWS[a]
Alcohols				
1-Decanol	20.5 ± 4.1	18.5 ± 3.8	35.4 ± 2.3	34.5 ± 1.6
2-Methyl-3-heptanol	12.8 ± 2.6[a,c]	46.1 ± 4.8[a,d,e]	11.5 ± 1.5[d,f]	74.5 ± 3.5[c,e,f]
Ethanol	47.4 ± 2.7[a]	851.1 ± 23.2[a]	11.0 ± 1.0[a]	231.8 ± 2.7[a]
1-Propanol	601.7 ± 1.8[a]	720.4 ± 0.8[a]	93.9 ± 5.6[a]	191.9 ± 3.4[a]
3-Ethyl-3-pentanol	14.2 ± 1.2	17.1 ± 2.0	16.3 ± 1.1	15.9 ± 0.8
Ketones				
2-Propanone	46.7 ± 2.3[c]	47.7 ± 3.3[e]	47.2 ± 1.2[f]	177.1 ± 6.0[c,e,f]
Acetophenone	263.1 ± 15.1[b,c]	278.9 ± 6.3[d,e]	64.9 ± 2.6[b,d,f]	19.8 ± 1.6[c,e,f]
2-Hexanone	787.3 ± 5.2[a]	830.9 ± 3.0[a]	55.3 ± 2.5[a]	86.8 ± 1.4[a]
2-Heptanone	20.5 ± 1.0[b]	12.6 ± 2.1[d]	72.3 ± 4.7[b.d.f]	22.4 ± 2.7[f]
2-Octanone	47.1 ± 1.7[a]	26.8 ± 2.2[a]	44.4 ± 2.3	30.6 ± 0.9
Aromatic compounds				
Benzene	884.6 ± 10.5[a,b]	930.7 ± 6.9[a,d,e]	906.0 ± 1.3[b,d]	890.9 ± 6.8[e]
1.3.5-Trimethylbenzene	21.3 ± 2.3[c]	6.9 ± 0.5[e]	14.7 ± 2.0[f]	89.8 ± 1.8[c,e,f]
o-Xylene	69.1 ± 0.8[b,c]	68.1 ± 1.0[d,e]	152.5 ± 6.0[b,d,f]	190.5 ± 8.4[c,e,f]
p-Xylene	51.2 ± 4.2[b]	45.8 ± 2.9[d]	172.8 ± 4.4[b,d,f]	37.0 ± 3.0[f]
Toluene	85.0 ± 1.4[b,c]	66.2 ± 2.5[d,e]	199.4 ± 2.6[b,d,f]	750.9 ± 1.8[c,e,f]
Sulfur compounds				
Ethanethiol	963.6 ± 7.0[a]	53.6 ± 0.2[a]	653.1 ± 5.5[a]	545.8 ± 1.3[a]
Dimethyl sulfide	43.9 ± 2.2[a]	14.9 ± 1.7[a]	222.9 ± 3.9[a]	650.8 ± 2.1[a]
Dimethyl disulfide	99.4 ± 3.9[a]	23.6 ± 2.1[a]	893.4 ± 5.5[a]	248.0 ± 0.4[a]
Diethyl disulfide	13.0 ± 1.2[b,c]	7.5 ± 0.9[d,e]	768.6 ± 1.8[b,d,f]	985.5 ± 4.7[c,e,f]
Methanethiol	2888.8 ± 4.8[a]	90.7 ± 1.2[a]	110.9 ± 1.9[a]	771.4 ± 1.8[a]

[a] Differences between PS and WAS

[b] Differences between PS and DGS

[c] Differences between PS and DWS

[d] Differences between WAS and DGS

[e] Differences between WAS and DWS

[f] Differences between DGS and DWS

among volatiles in each biosolid sample were indicated using small letter:

- The letter “a” indicates significant differences between primary sludge and waste-activated sludge (PS–WAS);
- The letter “b” indicates significant differences between primary sludge and digested sludge (PS–DGS);
- The letter “c” indicates significant differences between primary sludge and dewatered sludge (PS–DWS);
- The letter “d” indicates significant differences between waste-activated sludge and digested sludge (WAS–DGS);
- The letter “e” indicates significant differences between waste-activated sludge and dewatered sludge (WAS–DWS);
- The letter “f” indicates significant differences between digested sludge and dewatered sludge (DGS–DWS).

The letter “a” located within the same line indicates significant differences between all four types of biosolid samples.

Based on the data presented in Table 3, it can be stated that, within the chemical class of alcohols, only two compounds (ethanol and 1-propanol) exhibited statistically significant differences in composition of volatile fraction of the investigated biosolid cakes. 1-Propanol was proposed as a potential marker, because the presence of ethanol can result from numerous processes and operations, conducted not only in the wastewater treatment plants. 1-Propanol is one of the most frequently identified alcohols released from the biosolid cakes [24]. 2-Hexanone can be proposed as a potential marker from the ketones’ group. Similar to 1-propanol, it can be the marker allowing differentiation between various biosolid cakes.

In case of the statistical analysis of aromatic hydrocarbons, it is difficult to point a single compound, which could be a potential marker for biosolid cake differentiation. Toluene is the compound, which makes it possible to discriminate almost all investigated biosolid cakes—an exception is differentiation between primary and excess biosolid cakes, in which content of this substance is similar. Analogous situation occurs for the isomers of *o*-xylene and *p*-xylene. However, differentiation between primary and excess biosolid cakes is possible with benzene. It is worth emphasizing that the papers concerning measurement of the compounds emitted from the wastewater treatment plants show that toluene as well as isomers of xylene are the compounds characteristic for biosolid cake processing [24, 26].

The last group included in Table 3 is organosulfur compounds. Many papers on investigation of the biosolid cakes found these substances as key ones [25, 27, 28]. Performed statistical analysis revealed that methanethiol and ethanethiol could be the potential markers of particular types of the biosolid cakes. This statement is supported by the fact that remaining three compounds from the organosulfur group allow discrimination of most biosolid cakes, except for primary and excess ones.

Table 4 gathers concentrations of the odoriferous compounds, which were proposed, based on the statistical analysis, as potential markers of four types of biosolid cakes. Analysis of these data indicates that organosulfur compounds are characterized by relatively low concentrations as compared to the remaining compounds released from the biosolid cakes, especially in case of the excess cake. It can be also observed that the biosolid cakes after fermentation process exhibit higher content of organosulfur compounds than the excess cake. Literature explains this phenomenon by the fact that protein amino acids (for instance methionine), responsible for the production of organosulfur compounds in anaerobic conditions, are

Table 4 Concentration of key chemical compounds emitted from biosolid samples

Chemical compound	C ± SD/ppb				Odour description	OT/ppb [31]
	PS	WAS	DGS	DWS		
1-Propanol	23.0 ± 1.2	28.2 ± 1.3	3.9 ± 0.2	74.1 ± 2.9	Alcoholic, fruity, musty, pungent	94.0
2-Hexanone	19.5 ± 0.9	20.7 ± 1.1	1.4 ± 0.2	2.2 ± 0.1	Ethereal, fruity, cinnamon	24.0
o-Xylene	15.8 ± 0.7	15.6 ± 0.6	34.9 ± 1.7	43.7 ± 2.1	Fatty, geranium, oily, pungent	380.0
p-Xylene	11.7 ± 0.7	10.3 ± 0.5	39.5 ± 1.2	8.5 ± 0.4	Cold meat fat, sweet	58.0
Toluene	2.2 ± 0.1	1.7 ± 0.3	5.2 ± 0.3	19.5 ± 0.9	Ethereal, pungent, rubber, solvent,	330.0
Ethanethiol	3.7 ± 0.8	1.1 ± 0.1	2.5 ± 0.1	2.2 ± 0.1	Garlic-like, skunk-like, strong	0.0087
Dimethyl sulfide	1.6 ± 0.2	0.5 ± 0.1	8.5 ± 0.3	25.1 ± 1.5	Cabbage, mouldy, sulfurous	3.0
Dimethyl disulfide	2.5 ± 0.3	0.6 ± 0.1	22.7 ± 1.3	6.3 ± 0.7	Cabbage, onion, sulfurous, putrid	2.2
Diethyl disulfide	0.3 ± 0.1	1.5 ± 0.1	15.1 ± 1.3	19.4 ± 1.7	Poultry, cabbage, brussels sprout	2.0
Methanethiol	14.4 ± 1.0	0.5 ± 0.1	0.6 ± 0.1	3.9 ± 0.2	Cabbage, rotten egg, sulfurous	0.07

relatively durable and they do not undergo degradation [27, 29].

Seven out of ten chemical compounds emitted from the biosolid cakes (presented in Table 3) reveal higher concentration in dewatered cake than in fermented cake. It can be caused by a rapid growth of bacteria following cake dewatering, especially when this process is carried out in centrifuges (these devices are used in the treatment plants, from which the investigated samples of biosolid cakes were collected) [30].

Substantial differences were observed upon comparison of the results of VOCs emission from dewatered biosolid cakes originating from the treatment plants with different systems of water removal. One of them concerned aromatic hydrocarbons content in dewatered biosolid cakes—the cakes dewatered in a mechanical way using the centrifuges were richer in aromatic hydrocarbons than gravitationally dewatered cakes [24]. Another factors, which can have an influence on emission level of particular compounds from dewatered biosolid cakes, are the parameters of fermentation process (temperature and retention time) and, in the case of cake dewatering, amount of added flocculant, which facilitates separation of solid particles from liquid fraction via participation in aggregates' formation [29].

Table 4 also presents the values of olfactory threshold (OT), together with odour description. Olfactory threshold is the lowest concentration of each substance, which causes sensing of the smell with 50% probability. These data were used to determine theoretical odour concentrations for each of the four investigated types of biosolid cakes. The theoretical odour concentrations were calculated as a ratio of concentration of particular compound to its olfactory threshold. Figure 1 illustrates the results obtained in this way. The highest value of c_{od} was obtained for the primary cake, whereas the lowest one was for the excess cake. This situation is connected primarily with the concentration level of organosulfur compounds in these two types of biosolid cakes. Much higher content of those compounds is in the primary cake. Organosulfur compounds reveal very low values of olfactory threshold; hence, their contribution to strength of perceived odour is decisive. It is also the reason why dewatered cake exhibits higher odour concentration than fermented cake. One of the problems connected with the determination of concentration of organosulfur compounds emitted from the biosolid cakes is their instability. In the case of application of the solid sorbent-filled tubes, these compounds are released due to thermal desorption (at ca. 250–300 °C). At this temperature, thiols can be converted into sulfides. When thiols are present below LOD, it is reasonable to take advantage of summary concentration of organosulfur compounds not to omit contribution of such compounds as methanethiol or ethanethiol to strength of perceived odour [30, 32]. However, this approach hinders determination of the contribution of particular odorants because of different values of olfactory threshold.

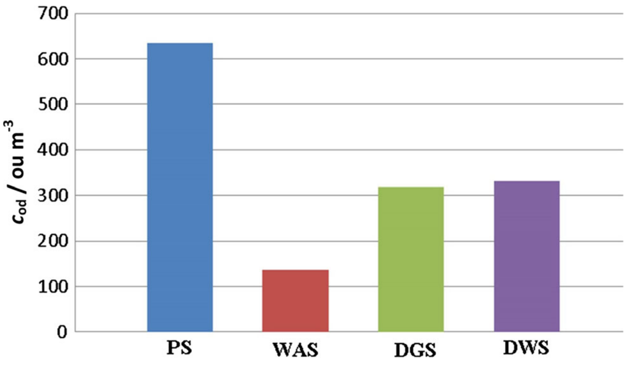

Fig. 1 Odor concentration of biosolid samples

Conclusions

Application of the methodology proposed in this paper, based on the GCxGC–TOF–MS technique and statistical analysis, allowed the determination of concentration of the volatile organic compounds, which could be potential markers for differentiation between four main types of biosolid cakes. Employed procedure was much less time-consuming mainly due to no need for quantitative analysis of all identified compounds, which in the case of gas samples is usually long and laborious step. Two-dimensional gas chromatography coupled with time-of-flight mass spectrometry technique makes it possible to define chemical composition of the samples with complex matrix, including such biological samples as the biosolid cakes. Utilization of numerical values of olfactory thresholds allows assessment of perceived odour strength of the biosolid cake samples, without olfactometric analyses. A disadvantage of the olfactometric approach is a need for team of trained assessors and suitable laboratory. The methodology presented in the paper can be an alternative to the existing solutions in the field of measurement of VOCs' emission level from the biosolid cakes.

Experimental

Biosolid sample collection

The biosolid samples were collected from the WWTP "Debogórze" located in Pomeranian Voivodeship, Poland. This facility is one of the biggest plants in this region and consists of three main technological sections: mechanical section, biological section, and sludge treatment section. Each day, 55,000 m^3 of sewage are supplied to this facility, 1.5 tons of waste are produced during mechanical treatment, and 31 tons of solid sludge are generated.

Four biosolid samples (primary sludge—PS; waste-activated sludge—WAS; digested sludge—DGS; and dewatered sludge—DWS) were collected in 20 dm^3 buckets and directly transported to a laboratory at the Gdansk University of Technology. Before measurements, the biosolid samples were stored at ambient conditions.

Instrumentation

To generate emission from the biosolid samples, the US EPA flux hood chamber was used. This device is widely utilized for identification of the chemical compounds emitted from various types of surfaces. Before each measurement, the biosolid samples were purged for 30 min using nitrogen gas with the flow rate 5 dm^3/min. The VOCs samples were collected for 10 min using the Tenax TA sorbent tubes (Gerstel, Germany), with the sampling flow rate 75 cm^3/min.

The chemical compounds emitted from the biosolid samples were determined using two-dimensional gas chromatography (Agilent Technologies, Palo Alto, CA, USA) equipped with a liquid nitrogen-based dual-stage cryogenic modulator and coupled with Pegasus IV time-of-flight mass spectrometer (LECO Corp., St. Joseph, MI, USA). Equity 1 capillary column (30 m × 0.25 mm × 0.25 μm film, Supelco) was used as a primary column; SGWAX capillary column (2.0 m × 0.1 mm × 0.1 μm film, Agilent Technologies) was used as the second column. A modulation period of 5 s was employed. To separate all chemical components present in the samples, the following optimized temperature program was used: for the first GC oven: initial temperature of 40 °C maintained for 1 min, then ramped at 10 °C/min–90 °C and at 3 °C/min–240 °C, and, finally, kept constant for 5 min; for the secondary GC oven, the optimized temperature program was with the shift of + 5 °C regarding the program of the primary GC oven. Hydrogen at a constant flow rate 1 cm^3/min was used as a carrier gas. The total analysis time was 45 min. Ions in the $m/z = 40–500$ range were analysed. The detector voltage was set to 1600 V and the temperature of the ion sources and the transfer line were maintained at 250 °C.

Data analysis

Analysis of the data obtained with the GCxGC–TOF–MS system was performed using the algorithm for peak deconvolution (with signal-to-noise setup at 100), included in the Chroma TOF software (LECO Corp., USA, version 4.44) Tentative identification was accomplished based on the selected fragmentation ions listed in the NIST 2011 Mass Spectral Library v. 2.0).

Statistical analysis

To determine the differences between volatile compounds emitted from various types of biosolids samples, two-way analysis of variance (ANOVA) was performed. Tukey's honest significant difference test (HSD Tukey's test, $p < 0.05$) was applied to compare the mean values of VOCs for different types of biosolid samples. The analysis was carried out using STATISTICA 12 software (StatSoft, Inc., Tulsa, Oklahoma, USA). Mean values and standard deviation (SD) were calculated from three repetitions for each biosolid sample.

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RESEARCH ARTICLE

Monitoring of odors emitted from stabilized dewatered sludge subjected to aging using proton transfer reaction–mass spectrometry

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Abstract

One of the potential emission sources of odorous compounds from wastewater treatment plants is sludge processing. The odorous compounds released from dewatered sludge can result in odor nuisance. This study concerns the use of flux hood chamber combined with proton transfer reaction—time of flight—mass spectrometry (PTR-MS) technique for periodical monitoring of odorous compounds emitted from aged, stabilized dewatered sludge samples from 2 different wastewater treatment plants located in Pomeranian Voivodeship, Poland. Based on determined concentration of the chemical compounds and olfactory threshold values, theoretical odor concentrations (known also as "odor activity value" or "odor index") were calculated for 17 selected odorous compounds. As a result, sulfur compounds such as diethyl sulphide, dimethyl sulphide, methanethiol, and ethanethiol were estimated as the most significant chemical compounds responsible for malodorous effect (average results, e.g., methanethiol, 178 ou/m^3; diethyl sulphide, 184 ou/m^3). Based on Pearson correlation coefficient, we revealed a correlation between odorous substances emitted from aged, stabilized dewatered sludge cakes. It was revealed that stabilized dewatered sludge still possessed significant amount of odorous compounds and applied measurement technique could be used for monitoring of odor concentration level of selected malodorous compounds.

Keywords Flux hood chamber · Odors · Proton transfer reaction–mass spectrometry · Sludge · Wastewater treatment plants

Introduction

Wastewater treatment plants (WWTPs) are one of the significant exemplifications of human activity, which have dominant impact on air quality, especially in the areas close to emission sources (Burlingame et al. 2004; Carrera-Chapela et al. 2014). They are a complex network of technological systems, consisting of many treatment stages, with different process conditions (Xu et al. 2014). Volatile organic compounds emitted from WWTPs, including odorous compounds, can have negative effect on people, animal, and plant ecosystem (Carrera-Chapela et al. 2016a; Gębicki 2016; Byliński et al. 2017b). One of the main sources of odorous compounds emission in WWTPs is sludge processing (Chen et al. 2011; Roy et al. 2011). The presence of VOCs in sludge has been attributed to the degradation of organic material (Adams and Witherspoon 2003). Over 36% of distribution of odor emission from WWTPs is from sludge dewatering, drying, and thickening processes (Gębicki et al. 2016). Among many odorous chemical compounds emitted from sludge cakes, volatile sulfur compounds (VSCs) are commonly considered to be the main substances causing odor nuisance from WWTPs (Carrera-Chapela et al. 2016b; Fisher et al. 2018b). This fact is related to relatively low values of olfactory threshold concentration of these compounds as compared to other volatile compounds (e.g., methanethiol, 0.07 ppb; ethanethiol, 0.0087 ppb as compared to toluene, 457 ppb; benzaldehyde, 42 ppb; or acetonitrile, 13,000 ppb) (Nagata

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2003). Emission of VSCs increases with the decrease in sludge oxygenation and increase in temperature during sludge treatment (Mrowiec et al. 2005). Sensory properties of odor mixtures can depend on their chemical composition. Even small modification in composition of the mixture can significantly change their sensory properties (Capelli et al. 2013a).

The products leaving anaerobic digesters, including digestate, which is a stock for dewatered sludge, are a source of odorants emission; it is necessary to process them in a way enabling their further utilization, for example in agriculture (Rosenfeld et al. 2001; Sharma et al. 2017). One of the most frequent operations is stabilization of sludge cakes—the stabilization process reduces organic matter, which leads to putrescibility, the overall microbe level increases, however the amount of pathogenic microbes decreases (Novak et al. 2003). This solution gains increasing popularity due to a possibility of biogas recovery, which is a source of renewable energy (Cieślik and Konieczka 2016). The process of sludge stabilization results in a decrease in the number of environmentally harmful substances, including those causing odor nuisance. Different approaches to the technical solutions in wastewater treatment plants, concerning conditions of the stabilization process, can influence on varying amount of odorous substances present in the sludge after the stabilization process (Qi et al. 2008; Kim et al. 2017). In order to decide about further utilization of stabilized sludge, it is necessary to determine a level of potential emission of the chemical compounds present in the sludge (Byliński et al. 2018). This evaluation can be carried out using mathematical models (Leyris et al. 2005; Lucernoni et al. 2016a) or via field measurements. In the latter case, direct measurements are a frequent solution, which employs devices enclosing investigated surface, which is a source of emission (Lucernoni et al. 2016b). Such approach is often used in the investigations concerning evaluation of wastewater treatments plants or landfills operation as far as analysis of emission level from particular elements of the installation is concerned. One of the advantages of direct measurements is a possibility of qualitative evaluation of emission from particular fragments of the emitting surface (so-called local emission). The direct measurements can provide emission rates from surfaces, rather than ambient emissions, which can be diffuse and difficult to monitor due to the influences of climate (Chen et al. 2017).

The devices used for direct determination of emission level of volatile odorous compounds can differ significantly because of applied construction design, shape, and dimensions of measurement chamber or conditions inside the chamber (Guillot et al. 2014). One of such solutions is flux hood chamber, the application of which to measurement of emission of volatile air pollutants was recommended by the United States Environmental Protection Agency (US EPA) (Klenbusch 1986). Operation of this chamber consists in generation of constant-composition mixture of volatile substances released from the samples under investigation. This is achieved by flushing with a stream of inert gas, for instance high purity nitrogen. Once uniform mixture is obtained, it is possible to sample the analytes using sorption tubes, bags, or other devices for gas samples collection (Hudson et al. 2009). The flux hood chamber is a device commonly used to measure emission of the odorous compounds generated in municipal wastewater treatment plants at particular stages of their operation (Hudson et al. 2008; Parker et al. 2013).

In order to identify and quantify odorous compounds present in gaseous samples, gas chromatography coupled with mass spectrometry (GC-MS) is commonly used (Nicolas et al. 2006; Bruno et al. 2007; Kosek et al. 2018). Typically in gas chromatography methods, a pre-concentration process is achieved by adsorbing volatile compounds from gaseous samples onto a suitable adsorbents. This pre-concentration step and desorption of analytes into the chromatographic column are time-consuming, which significantly elongates procedure (Byliński et al. 2017a; Woźniak et al. 2018). Although gas chromatography is the reference method for the analysis of VOCs in air samples, there is also growing need to develop new methods allowing direct, rapid, not time-consuming, non-invasive, and very sensitive monitoring of volatile compounds present in gaseous samples.

Among various available and investigated methods, there is proton transfer reaction–mass spectrometry technique (PTR-MS). This technique was development in the mid-1990s by Werner Lindinger group and it is based on the chemical ionization (Cappellin et al. 2012; Cui et al. 2016). The PTR-MS technique allows measurement of volatile analytes released directly from the investigated samples, without a need for complex operations of analytes enrichment. It is possible thanks to the fact that the volatile fraction is sucked directly into the ionization chamber. There occurs proton transfer reaction, only for the compounds, which exhibit higher affinity to proton than water. That is why presence of the main air components does not interfere with the results. Unquestionable advantage of the PTR-MS technique is a possibility of analytes measurement at very low concentration level (depending on spectrometer configuration, it is possible to achieve the detection level of ppb or even ppt *v*/*v*) (Jordan et al. 2009). PTR-MS technique is widely used in many applications: atmospheric chemistry, plant studies, food science, and medicinal applications (Hewitt et al. 2003; Biasioli et al. 2004; Tani et al. 2007; Blake et al. 2009). To the best of authors' knowledge, up till now, the PTR-MS technique has not been used for sludge cakes.

The objective for this study was investigation of the capability of proton transfer reaction–mass spectrometry technique for periodical monitoring of concentration of volatile organic compounds emitted from aging anaerobically stabilized sludge samples. Identification of the volatile organic compounds involved earlier application of the GC-MS technique as well as literature survey (Fisher et al. 2018a, c). This research can show changes in concentration of identified compounds, which can potentially contribute to odor nuisance from stabilized sludge cakes produced in WWTPs. This information can be useful to estimate a potential application of stabilized sludge in agricultural industry or other branches of human activity. Moreover, the PTR-MS technique allows evaluation odor activity values (OAV), describing which odorous compounds have the biggest contribution to strength of perceived odor of the entire gas mixture. Such situation enables optimization of the deodorization methods in order to reduce concentration of these compounds, which have the most significant impact on unpleasant odor generation.

Experimental

Site description and sampling location

Two wastewater treatment plants located in the northern part of Poland were selected for this investigation. Similar as other WWTPs, these facilities consist of three main technological sections: mechanical, biological, and sludge treatment sections. Figure 1 presents general configuration of WWTPs operation. Both processes of sludge stabilization occur in similar technological conditions; however, in the case of WWTP no.2, an additional stage was employed. It involved densification of sludge prior to forwarding them to anaerobic-mesophilic fermentation. Table 1 contains most important information about these treatment plants.

Stabilized dewatered sludge series were collected 6 times over a 3-month period. It means 1 series of 3 samples from each plant was collected every month on the same day. On this day, the samples were collected every 20 min. The total of 18 samples from both treatment plants were investigated. Sludge samples were collected in 20 L buckets, sealed with a lid and delivered at ambient temperature for emission analysis in the laboratory of the Gdansk University of Technology. Storage of the sludge cakes was carried out at ambient conditions (laboratory air temperature 20–25 °C).

Instrumentation

Determination of emission of volatile organic compounds from sludge cake samples was possible using Flux Hood Chamber combined with Proton Transfer Reaction Time Of Flight Mass Spectrometer (PTR-TOF-MS). This combination allows direct measurement of volatiles without any sample preparation. Figure 2 presents schematic diagram of flux hood chamber combined with PTR-TOF-MS.

Flux hood chamber

The equipment consists in Plexiglas chamber (dimension 16 in.) with carrier gas inlet and outlet line. On the top of the chamber, there are small holes allowing pressure release.

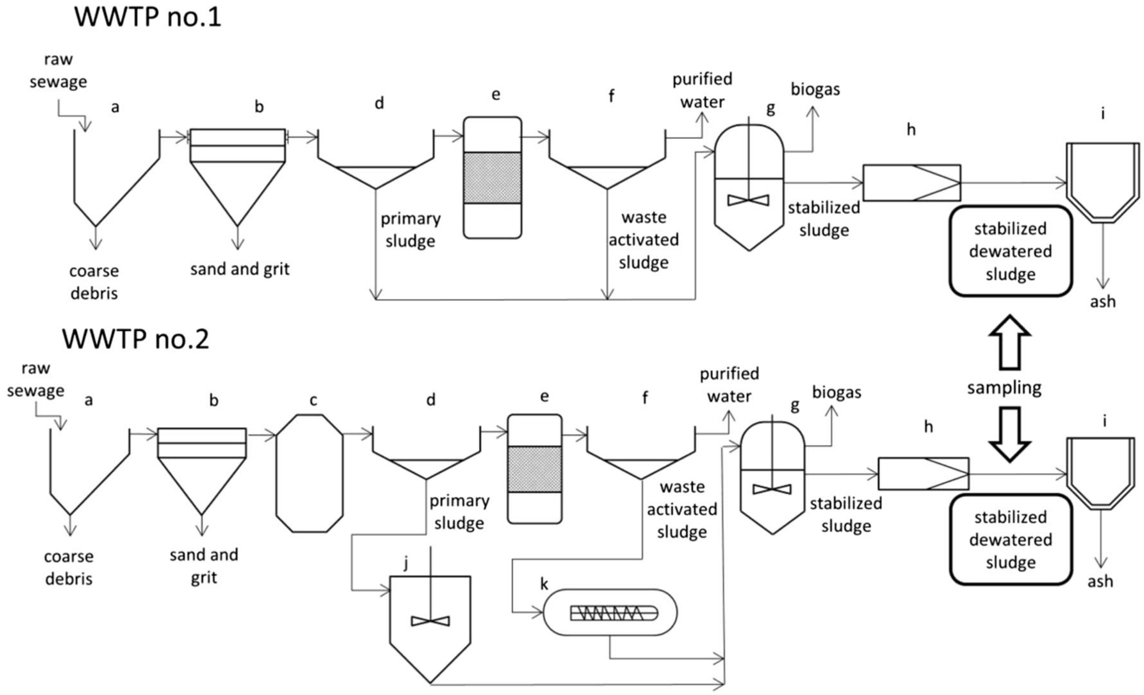


Fig. 1 Scheme of operation in WWTPs; a-screen; b-grit chamber; c-primary reaction chamber; d-primary clarifier; e-bioreactor; f-secondary clarifier; g-digester; h-thickener; i-combustion chamber; j-radial thickener; k-thickening centrifuge

Table 1 Details of wastewater treatment plants employed in the investigation

Location	WWTP no.1	WWTP no.2
Mechanical section	● 4 mechanical screens (two hook-belt screens with 6-mm clearance and two scraper screens with 10-mm clearance) ● 2 sand traps (30 m × 10.4 m × 4.5 m thickness) ● 3 primary settling tanks (diameter ca. 50 m)	● 3 hook screens (6-mm clearance) ● 1 sand trap ● 4 primary settling tanks (diameter ca. 36 m)
Biological section	6 bioreactors (summary 158,100 m^3) and secondary settling tanks	A block of biological reactors (summary 104.000 m^3) and 8 secondary settling tanks (diameter 42 m)
Sludge treatment	Anaerobic fermentation, temperature 37 °C, retention time 21–28 days	Anaerobic fermentation (36–38 °C, two closed fermentation chambers 5700 m^3 each), retention time 15–20 days, external pump mixing
Thermal treatment of sludge	Dewatering of sludge using sedimentation centrifuges; incineration of sludge occurs in a furnace with sand fluidized bed (temp. 850 °C); exhaust gases are subjected to purification processes	Drying of sludge–rotary drum dryer using superheated steam as a drying agent; incineration of dried sludge occurs in a furnace with fluidized bed (temp. 850–900 °C); exhaust gases are subjected to purification processes
Amount of supplied sewage (per day)	92,200 m^3	55,000 m^3
Amount of waste produce during mechanical treatment (per day)	3 tons	1.5 tons
Amount of solid sludge generated (per day)	140 tons	31 tons
Amount of biogas generated during fermentation (per day)	16,500 m^3	9500 m^3

During the investigation, the sludge samples were placed in buckets, in which they were transported from the treatment plants to a laboratory and stored between successive measurements. After opening the bucket, the sludge sample was enclosed in the flux hood chamber, in the way eliminating air movement between the chamber's and the bucket's walls (external wall of the flux hood chamber adhered to internal wall of the bucket). The chamber was mounted in this way during each measurement series. The samples were collected 3 times from every wastewater treatment plant; each time, 3 independent sludge specimens were taken for analysis. The amount of sludge collected was identical in each attempt. Before every measurement series, the sludge sample was stirred in order to ensure uniformity of the emitting surface. Prior to each measurement series, the sludge samples were purged for 30 min with a high purity nitrogen (flow rate 5 L/min, controlled using gas flow meter with no internal rubber parts).

PTR-TOF-MS measurements

Volatile organic compounds were detected in real time using proton transfer reaction—time of flight—mass spectrometry instrument (PTR-TOF-MS 1000 Ultra, Ionicon Analytik GmbH, Innsbruck, Austria). This system allows online measurement of volatile chemical compounds in the range of ppb *v*/*v* level. During each analysis, PTR-TOF-MS transfer line (1.2-m long, inner diameter of 1 mm (PEEK tubing, BGB Analytik AG, Switzerland)) was heated to 70 °C. The drift tube was kept under controlled conditions of pressure 2.6 mbar, temperature 70 °C, mass range of $m/z = 30$ to $m/z = 240$ Da and voltage 600 V, resulting in a field density ratio (E/N) of 122 Td (E being the electric field strength and N the gas number density; 1 Td = 10^{-17} Vcm^2). In order to record the mass spectra, IonTOF v. 2.4.40 software was used. Data processing was performed with PTR-TOF-MS Viewer v. 3.2.3.0. Tentative identification was performed based on the measured mass, isotopic ratios, and fragmentation spectra. Identified compounds were compared with the literature concerning composition of sludge samples (Fisher et al. 2017a). VOC concentration was calculated from peak areas, according to the formula described in the literature (Lindinger et al. 1998). The reaction rate coefficients used for quantification of analytes were based on the literature (Lindinger et al. 2001; Ammann et al. 2004; Zhao and Zhang 2004; Rinne et al. 2007; Taipale et al. 2008; Cappellin et al. 2012). When no data was available, the rate of $k_R = 2 \times 10^{-9}$ cm^3/s was used. Limit of quantification was set at 10× standard deviations of the background noise recorded for a blank sample (Konieczka and Namieśnik 2007).

Theoretical odor concentration

High concentration of particular substance present in gaseous samples does not always produce strong odor. One of the parameters, which can inform us about odor characteristic is olfactory threshold value (OT_i). Based on OT_i values for all quantified substances present in odorous gas mixture and their

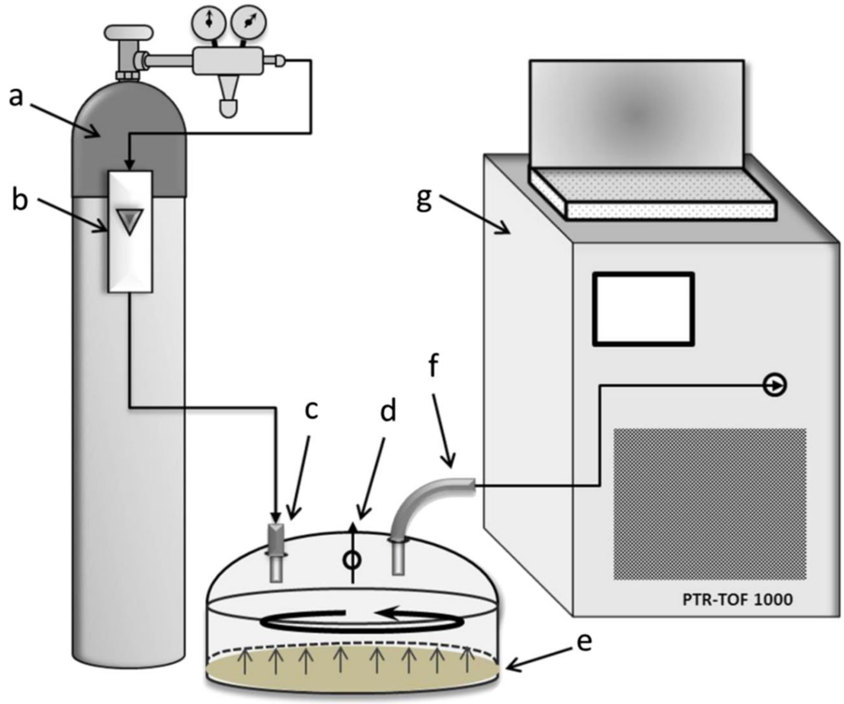


Fig. 2 Schematic diagram of flux hood chamber combined with PTR-TOF-MS (a-carrier gas (high purity nitrogen); b-gas flow meter; c-carrier gas inlet line; d-pressure release; e-sludge surface; f-sampling line; g-PTR-TOF-MS instrument)

chemical concentration values, it is possible to estimate odor activity value (OAV) of single odorous compounds (Eq. 1) and sum of theoretical odor concentrations of monitored compounds (Eq. 2):

$$\mathrm{OAV} = \frac{C_{\mathrm{i}}}{\mathrm{OT}_{\mathrm{i}}} \quad (1)$$

$$C_{\mathrm{od,OT}} = \sum_{i=1}^{n} \frac{C_{\mathrm{i}}}{\mathrm{OT}_{\mathrm{i}}} \quad (2)$$

where C_{i} is the analytical concentration of odorous compound i [ppbv], OT_{i} is the olfactory threshold concentration of compound i [ppbv], n is the number of compounds in the odorous mixture, OAV is defined as the odor activity value of single odorous compounds [ou/m^3] and $C_{\mathrm{od,OT}}$ is defined as sum of theoretical odor concentrations of monitored compounds [ou/m^3]. Based on the ratios between measured concentrations and olfactory threshold concentrations, a simple estimation of relative contribution of odor of sludge samples, in the absence of sensory measuring techniques, can be used. It must be emphasized that the theoretical odor concentration of mixture can differ from the value of odor concentration determined with dynamic olfactometry, for instance, due to presence of odor interaction effects (Byliński et al. 2017b).

Specific odor emission rates

Application of the flux hood chamber for measurement of emission of volatile odorous compounds, generated due to aging of sludge cakes, allows determination of a parameter known as specific odor emission rate (SOER). According to a definition, value of this parameter is a function of flow rate of the gas introduced to the measurement chamber, surface area of sludge being a source of emission and odor concentration determined for the investigated compounds (Capelli et al. 2013b). In the case of performed investigations, odor concentrations were not determined using dynamic olfactometry technique, commonly applied in this type of research. The values of odor concentration, adapted to calculation of SOER parameter, were determined instrumentally (see "Theoretical odor concentration" section), which is an alternative to the olfactometric approach and contributes to shortening of the time necessary for result acquisition. The values of SOER parameter, determined using theoretical odor concentrations of mixture, were calculated using the following equation (Eq. 3):

$$\mathrm{SOER} = \frac{C_{\mathrm{od,OT}} \times Q_{\mathrm{N}}}{A} \quad (3)$$

where SOER, specific odor emission rate [ou/m^{2}s]; $C_{\mathrm{od,OT}}$, sum of theoretical odor concentrations of monitored compounds [ou/m^3]; Q_{N}, flow rate of nitrogen into chamber [m^3/s]; and A, surface area enclosed by the chamber [m^2].

Statistical analysis

Statistical analysis was carried out using SPSS Statistics software (Version 21.0, SPSS Inc., Chicago, Illinois, USA). Analysis of correlation was conducted in order to determine dependences between concentration of particular compounds

Table 2 Average concentrations of tentatively identified compounds emitted from stabilized sludge cakes (*SD* standard deviations)

Tentatively identified compounds, protonated molecular formula, and protonated mass (amu)	Concentration (ppbv) ± SD									
	WWTP no.1					WWTP no. 2				
	1st day	7th day	10th day	14th day	21st day	1st day	7th day	10th day	14th day	21st day
Diethyl sulphide (DES) $(C_4H_{10}S)H^+$ (91.0576)	1.84 ± 0.09	1.43 ± 0.22	1.02 ± 0.31	1.01 ± 0.04	0.75 ± 0.04	6.08 ± 0.15	2.83 ± 0.88	2.24 ± 0.18	2.02 ± 0.27	1.95 ± 0.17
Dimethyl sulphide (DMS) $(C_2H_6S)H^+$ (63.0263)	18.67 ± 0.82	10.10 ± 0.90	11.07 ± 1.13	12.60 ± 1.13	2.43 ± 0.07	10.57 ± 9.43	12.20 ± 1.23	6.35 ± 3.81	5.23 ± 5.08	3.53 ± 1.08
Ethanethiol (ETH) $(C_2H_6S)H^+$ (63.0263)	0.44 ± 0.07	0.20 ± 0.01	0.21 ± 0.02	0.29 ± 0.02	0.24 ± 0.07	0.82 ± 0.10	0.31 ± 0.03	0.25 ± 0.04	0.21 ± 0.03	0.20 ± 0.06
Methanethiol (MTH) $(CH_4S)H^+$ (49.0107)	10.12 ± 0.31	4.15 ± 0.18	3.4 ± 0.21	3.05 ± 0.06	2.95 ± 0.15	12.43 ± 0.53	4.88 ± 0.74	4.55 ± 0.82	3.58 ± 0.65	2.91 ± 0.22
Acetonitrile (ACN) $(C_2H_3N)H^+$ (42.0338)	12.59 ± 0.76	12.09 ± 0.84	11.66 ± 0.83	10.82 ± 0.34	5.60 ± 0.19	5.46 ± 0.21	7.92 ± 0.10	6.65 ± 0.20	11.96 ± 1.06	13.17 ± 1.50
Pyridine (PIR) $(C_5H_5N)H^+$ (80.0495)	1.35 ± 0.04	1.33 ± 0.40	2.81 ± 1.38	0.47 ± 0.11	1.39 ± 0.02	2.91 ± 0.21	0.53 ± 0.10	0.31 ± 0.04	0.42 ± 0.08	0.75 ± 0.28
Benzene (BEN) $(C_6H_6)H^+$ (79.0542)	3.69 ± 0.34	3.57 ± 0.19	2.97 ± 0.35	1.69 ± 0.06	0.93 ± 0.12	10.48 ± 5.36	4.67 ± 0.70	2.13 ± 0.16	2.28 ± 0.16	3.13 ± 0.45
Toluene (TOL) $(C_7H_8)H^+$ (93.0699)	4.46 ± 0.32	2.99 ± 0.22	2.62 ± 0.55	1.57 ± 0.07	0.92 ± 0.08	26.35 ± 0.50	11.86 ± 0.94	13.35 ± 2.23	20.77 ± 1.80	24.96 ± 3.78
Xylene* (XYL) $(C_8H_{10})H^+$ (107.0855)	7.37 ± 0.48	15.18 ± 0.47	14.56 ± 2.04	7.98 ± 0.20	1.72 ± 0.15	5.29 ± 0.11	4.29 ± 0.51	4.69 ± 0.37	5.51 ± 0.50	5.61 ± 0.67
Cymene* (CYM) $(C_{10}H_{14})H^+$ (135.1168)	3.29 ± 0.14	2.37 ± 0.20	2.06 ± 0.35	1.82 ± 0.13	0.94 ± 0.03	6.14 ± 0.12	7.65 ± 0.83	4.84 ± 0.26	10.78 ± 1.30	10.38 ± 1.84
1,2,3-trimethylbenzene (TMB) $(C_9H_{12})H^+$ (121.1012)	4.50 ± 0.18	3.38 ± 0.24	3.03 ± 0.47	2.02 ± 0.12	1.08 ± 0.07	5.08 ± 0.08	5.25 ± 0.60	3.95 ± 0.22	7.00 ± 0.71	7.06 ± 1.02
1-propanol (PRO) $(C_3H_8O)H^+$ (61.0648)	34.94 ± 2.96	17.55 ± 0.90	11.05 ± 1.52	6.67 ± 0.39	5.25 ± 1.04	27.09 ± 1.24	23.52 ± 3.49	12.97 ± 1.07	12.56 ± 1.99	21.64 ± 4.75
Ethanol (ETN) $(C_2H_6O)H^+$ (47.0491)	10.64 ± 0.18	13.86 ± 0.39	11.83 ± 1.46	10.48 ± 6.57	12.12 ± 1.33	22.19 ± 1.66	21.49 ± 1.78	18.68 ± 0.83	16.53 ± 1.24	22.29 ± 2.24
Acetaldehyde (ACA) $(C_2H_4O)H^+$ (46.0413)	7.87 ± 0.67	7.20 ± 0.90	7.76 ± 0.57	9.58 ± 1.09	6.23 ± 0.57	27.21 ± 0.94	18.75 ± 2.24	15.83 ± 0.52	19.98 ± 1.04	23.08 ± 1.72
Benzaldehyde (BZA) $(C_7H_6O)H^+$ (107.0491)	6.54 ± 0.38	13.81 ± 0.59	13.33 ± 1.10	7.09 ± 0.50	1.52 ± 0.19	4.80 ± 0.19	3.78 ± 0.50	4.08 ± 0.38	4.84 ± 0.60	5.27 ± 0.71
Acetone (ACT) $(C_3H_6O)H^+$ (59.0491)	23.51 ± 1.50	9.93 ± 1.83	8.41 ± 1.05	6.12 ± 0.77	5.52 ± 0.74	37.91 ± 2.15	33.82 ± 2.64	27.72 ± 3.46	23.30 ± 1.38	33.89 ± 1.39
α-pinene (PIN) $(C_{10}H_{16})H^+$ (137.1325)	13.92 ± 0.67	7.65 ± 0.76	5.39 ± 0.83	3.01 ± 0.11	2.29 ± 0.13	14.05 ± 0.25	20.88 ± 1.47	13.93 ± 0.80	33.27 ± 2.91	33.13 ± 2.05

*Mixture of isomers of these compounds

Table 3 Example of calculation of OAV (sludge sample from WWTP no 2. at 1st day of storage).* olfactory threshold was calculated as average of olfactory threshold for 3 isomers of this compound

Name of compound	Odor description	OT$_i$ [ppbv] (Nagata 2003)	OAV [ou/m^3]		
			Minimum	Maximum	Average
Diethyl sulphide	Sulfurous, onion, leek,	0.033	179.7	188.8	184.2
Methanethiol	Cheese, cooked cabbage, fishy, garlic, gasoline, meaty, rotten egg, sulfurous	0.07	170.1	185.1	177.6
Ethanethiol	Garlic-like, skunk-like, strong	0.0087	82.5	105.0	93.8
Acetaldehyde	Ethereal, fresh, fruity, pungent	1.5	17.5	18.8	18.1
Dimethyl sulphide	Cabbage, fruity, gaseous, gasoline, moldy, sulfurous, vegetable soup	3	13.5	14.2	13.9
Acetone	Characteristic, sweetish, fragrant	42,000	< 1		
Acetonitrile	Aromatic, characteristic, sweet, ethereal	13,000	< 1		
Cymene	Balsamic, citrus, fruity, fuel gasoline, herbaceous, lemon, solvent, spicy, sweet	7165*	< 1		
Benzene	Paint thinner	2700	< 1		
Ethanol	Alcoholic, pungent, sweet	520	< 1		
Toluene	Caramelized, ethereal, fruity, paint, pungent, rubber, solvent,	457	< 1		
Xylene	cold meat fat, plastic	380*	< 1		
α-pinene	Camphor, citrus, fruity, green, lime, pine, sweet, terpenic, turpentine, woody	180	< 1		
1,2,3-trimethylbenzene	Characteristic, distinctive, aromatic	120	< 1		
1-propanol	Alcoholic, fruity, musty, plastic, pungent	94	< 1		
Pyridine	Cold meat fat, fishy, rancid	63	< 1		
Benzaldehyde	Almond, burnt sugar, fruity, woody	42	< 1		
$C_{od,OT}$			463.9	512.6	488.3

emitted from stabilized sludge cakes. Determined correlations were meant to pertain to all monitored compounds as well as to particular groups of chemical compounds. Special attention was paid to the correlations occurring in case of both samples of sludge cakes. The values of Pearson correlation coefficient were determined for significance levels 95% and 99%.

Results and discussion

Concentration of VOCs emitted from sludge

The chemical concentrations of 17 volatile compounds emitted from aged, stabilized sludge samples from two different wastewater treatment plants are shown in Table 2.

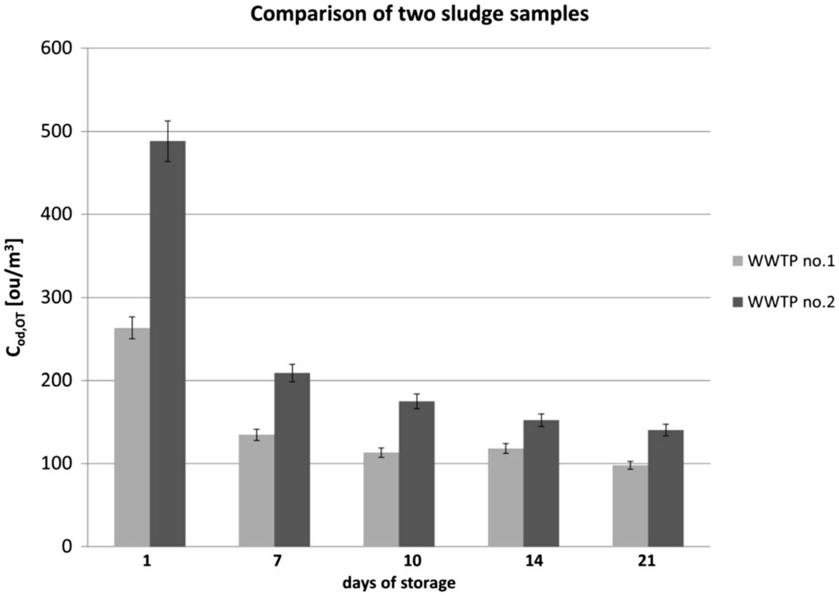
Chemical compounds present in this table were selected as the main odorous compounds emitted from sludge cakes based on the available literature (Rosenfeld et al. 2001; Fisher et al. 2017a, b) and quantitative analysis of sludge samples using thermal desorption-gas chromatography coupled with mass spectrometry technique.

Composition of volatile fraction from flux hoods headspace of the sludge cakes was changing significantly during execution of the investigation. The highest concentrations, determined during the measurements conducted on the day of sludge collection from the treatment plant, were observed for:

- the sludge sample from the treatment plant no. 1 for dimethyl sulphide, 1-propanol, and acetone; they were at the level of 18–35 ppbv,
- the sludge sample from the treatment plant no. 2 for dimethyl sulphide, acetone, benzene, toluene, 1-propanol, and acetaldehyde; they were at the level of 26–40 ppbv.

In case of the sludge sample from the treatment plant no. 2, the concentrations were significantly higher for most of the monitored compounds. For example, 14 out of 17 compounds exhibited higher concentration on the first day of measurements. It was observed that concentration of some compounds decreased during the entire 21-day measurement cycle. The examples are 1-propanol and cymene for the sludge from the treatment plant no. 1 or ethanethiol and diethyl sulphide for the sludge from the treatment plant no. 2. In the other cases, it was noticed that on the seventh day since the sample collection concentration of a given compound was substantially lower than on the first day of measurements, however, the differences in concentration between the seventh and twenty-first day were not so significant (for instance acetone, methanethiol for sludge from the treatment plant no. 1 or

Fig. 3 Average values of sum of theoretical odor concentrations of monitored compounds ($C_{od,OT}$) estimated for 2 sludge cakes during 3 weeks

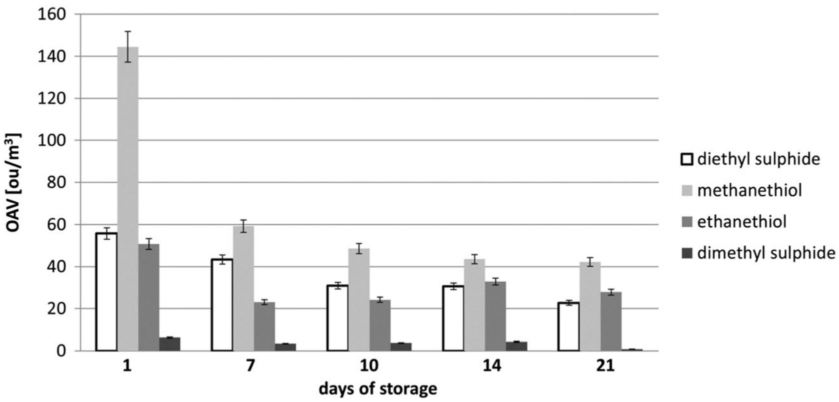


benzene and methanethiol for the sludge from the treatment plant no. 2). In the case of some compounds, the concentrations underwent small fluctuations throughout the period of investigation (for example acetaldehyde and ethanethiol for the sludge from the treatment plant no. 1 or benzaldehyde for the sludge from the treatment plant no. 2).

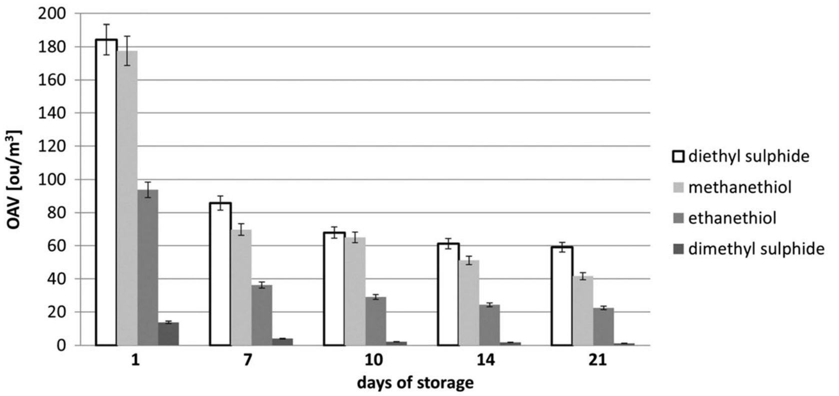
Composition of volatile fraction of stabilized sludge cakes subjected to aging can differ depending on the origin of particular sludge sample. Both treatment plants also differ in selected technological parameters (see Table 1), for instance, time of sludge retention at the anaerobic stabilization stage (Lewkowska et al. 2016). Site planning around the plant can

Fig. 4 Odor activity values for 4 identified compounds; **a** sludge cake from WWTP no. 1, **b** sludge from WWTP no. 2

a) sludge from WWTP no. 1



b) sludge from WWTP no. 2



play an important role in composition of sludge. In heavy industrialized regions with the facilities lacking wastewater treatment plants, composition of wastewater can be especially rich in the compounds characteristic for an operation profile of particular facility (Fisher et al. 2017b). In the case of dominant contribution of households or residential areas, a profile of wastewater supplied to a treatment plant will be completely different (Alvarez et al. 1999). It should be emphasized that the PTR-MS technique allowed identification and measurement of ethanethiol and methanethiol, the compounds which are easily converted to sulphides upon measurements with other methods (Gruchlik et al. 2013)

Theoretical odor concentration

Tentatively identified compounds present in Table 2 can have different impact on odor nuisance associated with treatment of sludge cakes. These compounds have different odor properties, which also depend on composition of odorous mixture and some external factors (air temperature and humidity, intensity of solar radiation). In order to define which of these compounds have most significant impact on unpleasant smell, odor activity value for each compound (OAV) and sum of theoretical odor concentrations of monitored compounds ($C_{od,OT}$) were calculated. In Table 3, an example of calculation of OAV and $C_{od,OT}$ was shown. In Fig. 3, a summary of $C_{od,\ OT}$ was compared taking into account type of WWTP and measurement day.

Based on the results presented in Table 3 and Fig. 3, it can be observed that strength of perceived odor differed for both samples, although this difference diminished with time as far as given measurement day is concerned. The highest values of sum of theoretical odor concentrations of monitored compounds were determined on the day of the samples collection from the plants. Storage and aging of the sludge resulted in a decrease in odor concentrations. It can also be noticed that the rate of sum of theoretical odor concentrations of monitored compounds decrease diminished after 10 days and stabilized as far as the samples collected from wastewater treatment plant are concerned. However, obtained values were still at the level of 100 ou/m^3, which means significant exceeding of the admissible levels accepted in many countries with strict policy regarding emission of odorous compounds (Bokowa 2010; Van Harreveld et al. 2013; Guillot and Milan 2016).

Comparison of the sum of theoretical odor concentrations of monitored compounds reveals that in case of every measurement day, $C_{od,OT}$ values of the sludge collected from the treatment plant no. 2 were higher than the one determined for the sludge from the treatment plant no. 1. Such situation can suggest two dominant technological issues. Firstly, the wastewater treatment plant no. 1 processes bigger amount of wastewater, which leads to dilution of the entire contaminants load, thus to dilution of the odorous compounds. Secondly, duration of anaerobic fermentation in a technological process of the treatment plant no. 1 is longer, which allows transfer of bigger amount of volatile organosulphur compounds and volatile organic compounds to biogas. The data presented in Table 3, concerning the values of olfactory threshold of particular odorants and OAV determined for them, suggest that organosulphur compounds (methanethiol, ethanethiol, methyl sulphide, diethyl sulphide) had the biggest influence on summary odor concentration. These compounds are characterized by relatively low values of olfactory threshold, which implies that they can have a dominant impact on strength of perceived odor, even if they are present at low concentration level. Figure 4 illustrates changes of OAV for four aforementioned compounds during the entire period of the investigation. Analysis of these data reveals that methanethiol (in case of the treatment plants no. 1 and no. 2) and diethyl sulphide (in case of the treatment plants no. 2) exhibited the biggest influence on the level of perceived odor.

Table 4 Specific odor emission rates for sludge samples and other literature examples

		SOER [ou/m^{2}s]				
Days of storage:		1st	7th	10th	14th	21st
Stabilized biosolids samples	WWTP no. 1	0.157 ÷ 0.180	0.078 ÷ 0.094	0.062 ÷ 0.082	0.072 ÷ 0.079	0.056 ÷ 0.069
	WWTP no. 2	0.297 ÷ 0.328	0.102 ÷ 0.165	0.099 ÷ 0.125	0.073 ÷ 0.122	0.058 ÷ 0.121
Literature examples						
Sources of emission	Type of chamber		SOER [ou$_E$/m^{2}s]			ref.
Municipal solid waste landfills	Wind tunnel		2.1 ÷ 8.9			(Sironi et al. 2005)
	"LabOlf" sampling device (homemade)		0.011			(Lucernoni et al. 2016b)
Agricultural odor sources	Flux hood chamber Wind tunnel		0.194 ÷ 1.973 13.47 ÷ 229.0			(Hudson et al. 2009)
Livestock facilities	Wind tunnel	Polypropylene cover	1.3 ÷ 2.1 12.2 ÷ 57.0			(Hudson et al. 2006, 2008)
	Wind tunnel	Straw cover	0.5 ÷ 4.6 3.3 ÷ 39.7			

Emission from sludge cakes

The information concerning concentration changes of particular compounds due to aging of stabilized sludge cakes and corresponding OAV odor concentrations constitutes valuable data reflecting possible changes of odor character of sludge cakes. Defining of potential influence of odorants released to the environment should also take into account the factors connected with the rate of release and propagation of the odorants.

In order to determine emission level of volatile odorous compounds, two equipment solutions are most commonly employed–flux chamber, utilized in the investigations described in this paper, and wind tunnel system. Fundamental difference between these two devices is connected with geometrical parameters and internal circulation of the gas flushing an odorant-emitting surface. Application of these solutions allows evaluation of odorants emission level defined as SOER. Table 4 gathers the values of SOER parameter obtained for the samples of sludge cakes during the investigation of odorous compounds emission as well as some literature examples determined for different potential sources of odorous compounds emission, taking into account type of the chamber used for odorants emission measurement.

Based on the emission of odorous compounds illustrated in Table 4, it can be stated that higher values were obtained for the sludge originating from the treatment plant no. 2, which is a consequence of higher values of OAV identified in the samples collected from this plant. Analogously, it was observed the value of SOER parameter also decreased upon aging of the samples.

Evaluation of emission of the odorous compounds released from different industrial and municipal sources can be an indicator of environmental impact of particular facility (Wu et al. 2017). Different values of odorous compounds emission can be obtained depending on type of odorants emission sources, methodology of investigation, and design solutions applied (geometrical dimensions, type of utilized material, circulation of gas stream inside the chamber)—selected examples are presented in Table 4. The information presented shows that magnitude of the SOER parameter is strongly diversified, both within single emission source as well as type of measurement chamber. In majority of cases, literature values are higher than these calculated for sludge cake samples. This difference can stem from a couple of factors. In the case of literature data, odorant emission level was calculated based on the odor concentrations evaluated using dynamic olfactometry technique, being a reference method in olfactometric investigations. In our studies, OAV were determined only on the basis of concentrations of particular compounds and their olfactory thresholds, which could have influenced on lower values of odor concentrations and thus on lower values of odorants emission. Instrumental investigations do not take into consideration the effect of odor interactions (for example odor synergism), but only sum of odor concentrations of particular compounds (Gębicki 2016). Moreover, the investigation engulfed only 17 odorous compounds, whereas holistic examination using dynamic olfactometry does not impose any limitation as far as the number of compounds in odorous mixture is concerned. Furthermore, in many cases, odorants emission level is determined with respect to “in situ” process, not to the material obtained as a product of selected unit process (Byliński et al. 2017a). Prior to the measurements, the sludge samples were transported to a laboratory, which could also have an influence on lower concentration of odorants determined during the analyses.

Statistical analysis

In order to describe mutual dependences between concentrations of particular compounds present in volatile fraction of stabilized sludge cakes, the numerical values of Pearson correlation coefficient were determined and included in Table 5, together with the concentration values obtained for both treatment plants. These data indicate strong, positive correlations between some compounds belonging to the same class of chemical compounds, especially organosulphur compounds:

- Methanethiol revealed strong, positive correlation with ethanetiol and diethyl sulphide (in case of the sludge from the treatment plant no. 1 $r^2_{\mathrm{I}} = 0.993$, $r^2_{\mathrm{I}} = 0.896$, respectively, in case of the sludge from the treatment plant no. 2 $r^2_{\mathrm{II}} = 0.996$, $r^2_{\mathrm{II}} = 0.994$) and dimethyl sulphide with diethyl sulphide ($r^2_{\mathrm{I}} = 0.827$, $r^2_{\mathrm{II}} = 1000$).
- Strong, positive correlation was noticed between dimethyl sulphide and ethanethiol and methanethiol (in case of the sludge from the treatment plant no. 2 $r^2_{\mathrm{II}} = 0.998$ and $r^2_{\mathrm{II}} = 0.994$, respectively, however $r^2_{\mathrm{I}} = 0.723$, $r^2_{\mathrm{I}} = 0.765$).

Obtained information about high values of correlation coefficients indicates similar character of concentration changes of particular substances from the organosulphur compounds group due to sludge aging. Similar dependence was also observed in case of the investigations concerning emission of odorous compounds from 9 different regions of a landfill (Fang et al. 2012). A strong correlation within investigated groups of compounds, also including organosulphur ones, was observed based on analysis of linearity of identified compounds behavior. Additionally, a correlation between the investigated groups of compounds was evident, which could be a result of transformations of particular groups of compounds into the other ones.

In the case of aromatic hydrocarbons, a positive correlation was observed for both sludge samples, but only between a mixture of xylenes and benzaldehyde ($r^2_{\mathrm{I}} = 1000$ and $r^2_{\mathrm{II}} =$

Table 5 Pearson correlation coefficients between different odorous compounds emitted from sludge cakes ($n = 5$, 1st line concerns WWTP no. 1 and 2nd line, WWTP no. 2)

	ACN	ACA	MTH	ACT	PRO	ETH	BEN	TOL	BZA	PIN	TMB	ETN	XYL	CYM	DMS	PIR	DES
ACN	1	.534	.490	.558	.627	.292	.881*	.802	.746	.669	.868	.049	.756	.872	.863	.120	.747
		− .030	− .734	− .310	− .294	− .688	− .600	.281	.600	.981**	.904*	− .205	.590	.931*	− .689	− .504	− .691
ACA		1	.039	.040	.009	.294	.079	.100	.195	.011	.168	.832	.208	.298	.610	− .397	.137
			.684	.927*	.745	.737	.809	.884*	.654	.038	.330	.575	.584	.170	.731	.874	.734
MTH			1	.995**	.968**	*.883**	.631	.871	− .084	.950*	.808	− .349	− .075	.850	.765	− .051	*.896**
				.862	.631	*.996***	.982**	.407	.025	− .658	− .403	.409	.014	− .528	*.994***	.949*	*.994**
ACT				1	.985**	.840	.704	.916*	.016	.974**	.862	− .385	.024	.890*	.790	.020	.921*
					.617	.886*	.935*	.814	.527	− .247	.042	.428	.502	− .126	.872	.967**	.874
PRO					1	.753	.796	.955*	.141	.997**	.913*	− .417	.150	.926*	.784	.026	.968**
						.686	.698	.385	.101	− .244	− .009	.905*	− .046	− .109	.699	.725	.705
ETH						1	.269	.597	− .402	.711	.527	.027	− .390	.642	.723	− .329	.672
							.993**	.455	.073	− .610	− .344	.464	.050	− .474	*.998***	.969**	*.999***
BEN							1	.928*	.710	.837	.959**	− .405	.716	.903*	.721	.312	.858
								.559	.193	− .524	− .245	.481	.165	− .387	.988**	.991**	.990**
TOL								1	.415	.974**	.992**	− .407	.423	.977**	.838	.199	.955*
									.920*	.308	.537	.296	*.889**	.377	.432	.654	.436
BZA									1	.213	.518	− .118	*1.000***	.421	.317	.457	.284
										.591	.727	.107	.979**	.604	.046	.308	.051
PIN										1	*.939**	− .437	.221	*.942**	.792	.082	.971**
											.954*	− .238	.597	*.982***	− .603	− .436	− .609
TMB											1	− .351	.526	.981**	.854	.213	.938*
												− .079	.720	.983**	− .336	− .148	− .343
ETN												1	− .108	− .202	.123	− .670	− .277
													− .083	− .173	.462	.529	.478
XYL													1	.432	.331	.445	.295
														.607	.024	.267	.025
CYM														1	.924*	.048	.962**
															− .460	− .302	− .469
DMS															1	− .082	*.827*
																.961**	*1.000***
PIR																1	− .086
																	.964**
DES																	1

Italicized entries show the strongest correlation between chemical compounds

ACN acetonitrile, *ACA* acetaldehyde, *MTH* methanethiol, *ACT* acetone, *PRO* 1-propanol, *ETH* ethanethiol, *BEN* benzene, *TOL* toluene, *BZA* benzaldehyde, *PIN* α-pinene, *TMB* 1,2,3-trimethylbenzene, *ETN* ethanol, *XYL* xylene, *CYM* cymene, *DMS* dimethyl sulphide, *PIR* pyridine, *DES* sulphide diethyl

* $P < 0.05$ (2-tailed)

** $P < 0.01$ (2-tailed)

0.979). For the remaining groups of compounds, only single, strong correlations were noticed between concentrations of the compounds belonging to the same chemical group. That is why, it is difficult to state, based on the investigations presented in this paper, that changes of concentration of the compounds, except of organosulphur ones, are correlated in a linear way. Obviously, one has to remember about small number of the investigated compounds, however they play an important role from the point of view of odor nuisance associated with processing of sludge cakes.

Conclusions

The paper presents the attempt to apply the flux hood chamber coupled with proton transfer reaction–mass spectrometry technique for periodical monitoring of concentration changes of selected odorous compounds released during aging of stabilized and dewatered sludge cakes originating from two wastewater treatment plants. Combination of these solutions allowed determination of concentration changes of 17 odorous compounds released from the sludge cakes. Based on literature values of olfactory thresholds of the investigated compounds, it was revealed that organosulphur compounds (independently on the progress of sludge aging) had the biggest contribution to an increase in odor intensity connected with sludge cakes processing, in spite of the fact that their concentrations are lower than the ones of the other substances emitted from the sludge cakes. It was shown that even after 21 days of sludge aging, the sum of theoretical odor concentrations of monitored compounds still possessed significant load of odorous contaminants; the level of evaluated concentration was ca. 100 ou/m^3. Moreover, it was found, comparing obtained results with literature data, that the results acquired with various types of chambers for measurement of volatile odorous compounds emission can differ between each other. These differences can result from flow rate of gas supplied to the chamber or construction design of the chamber, for example, implementation of internal mixing. It was also shown that in the case of organosulphur compounds, one could see correlations between concentrations of particular compounds belonging to this group.

Presented methodology of measurement of volatile odorous compounds employing the flux hood chamber coupled with PTR-TOF-MS technique allows monitoring of concentration of these compounds in real time. It enables collection of big amount of data without a need of time-consuming and expensive operations connected with preparation for analysis. So far, the PTR-MS technique has not been employed to monitoring of dewatered sludge. As compared to the GC-MS technique with thermal desorption, it is characterized by significantly shorter time of a single analysis and no need for sample preparation prior to analysis, which is in accordance with the green chemistry principles. Moreover, it excludes application of various types of sorbents for analytes sampling, which obviously influences on the final results of quantitative measurements (elimination of additional measurement errors). It seems that among other instrumental techniques, the PTR-MS can be one of the most effective approaches to real-time monitoring of concentration changes of particular odorous compounds. Nevertheless, it must be emphasized that dynamic olfactometry technique is the reference method, which provides holistic measurement of the entire mixture, not of its particular components, and takes into account odor interactions, for example, synergism.

The relatively high OAV of organosulfur compounds emitted from the sludge cakes cause an issue with the further utilization of the stabilized sludge. One could assume that after the unit processes depicted in Fig. 1, the content of these compounds ought to be characterized by significantly lower values of OAV. However, since their thermal utilization leads to the further emission of pollutants into the atmosphere in the form of sulfur dioxide, the improvement of the methane fermentation process through the disintegration of concentrated sludge seems to be a valid approach. The optimization of the parameters of these unit operations will result in a lower concentration of organosulfur compounds in the stabilized sludge, thus reducing the emission of odors.

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Article

Evaluation of Health Hazard Due to Emission of Volatile Organic Compounds from Various Processing Units of Wastewater Treatment Plant

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† Prof. Jacek Namieśnik passed away on the 14 April 2019. You will always remain in our memory.

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Abstract: The paper describes an attempt at health risk assessment and odour concentration determination in the most important units of a wastewater treatment plant. The cancer risk (CR) and hazard index (HI) parameters in selected measurement locations were calculated based on the results of chromatographic analyses (GCxGC-TOF-MS) and the United States Environmental Protection Agency (US EPA) guidelines. No exceedance of the CR and HI acceptable levels was observed for identified and quantitatively determined compounds from the VOCs group. The acceptable level was exceeded for the summary HI parameter. Following a classification of the International Agency for Research on Cancer (IARC), it was noticed that the highest hazard was connected to the presence of formaldehyde belonging to group 1—the compounds regarded as carcinogenic. Based on the olfactometric analyses, it was estimated that the highest odour concentration, 37.2 ou/m^3, occurred at the solid waste composting piles. It was also revealed that an increase in odour concentration corresponded to a higher health risk for employees of the wastewater treatment plant, due to exposure to volatile odorous compounds. Accordingly, this method of odour measurement can be a fast indicator describing health risk level.

Keywords: wastewater treatment plant; odour concentration; health risk; odour emission; odour

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1. Introduction

Municipal wastewater treatment plants (WWTPs), despite their beneficial contribution to environmental protection, are recognised as one of the potential emission sources of atmospheric pollutants [1–4]. The main group of compounds emitted from the treatment plants are volatile organic compounds [5,6]. Their presence in ambient air can result in the discomfort of the plant's employees as well as the residents of neighbouring areas, even when those compounds are present at very low concentration levels. Moreover, some of these compounds can cause a number of psychosomatic symptoms such as anxiety, stress, headache and dizziness, nausea, loss of consciousness. The odorous substances characterised by low olfactory threshold can have significant impact on discomfort associated with the perception of unpleasant odour of different intensity and hedonic tone [7,8].

Wastewater directed to particular treatment stages can differ in chemical composition [9]. That is why the type and amount of volatile odorous compounds generated at any given wastewater and sludge treatment stage can differ substantially. At the beginning, the wastewater stream is usually subjected to mechanical treatment where solid waste, grease and small mineral fractions are removed. These operations frequently produce many volatile odorous compounds. A solid fraction isolated during the mechanical treatment is rich in various precursors of odorous compounds, so it is important to select proper methods of its further processing (stabilisation, composting or incineration) [10]. Lower levels of odorants emission are observed in case of separation of wastewater from sludge in the preliminary settling tanks. It is due to the fact that at this stage no operations of mechanical separation of solid fractions are carried out (separation occurs via sedimentation and flotation) [11]. A number of metabolic processes take place in the biological reactors; they proceed in aerobic and anaerobic conditions, in presence of microorganisms. These processes are often accompanied by a release of the odorous compounds. Their emission can be limited by the introduction of bacterial strains, which neutralise selected groups of odorous compounds [12]. However, it is necessary to provide and maintain suitable conditions, ensuring efficiency of biological removal of nitrogen and phosphorus. After leaving the biological reactors, the stream of wastewater and biological sludge enters the secondary settling tanks where separation occurs. At this stage, wastewater is usually lean in the odorous compounds. The substances, which can contribute to odour include: 2,4,6-trichloroanisole, geosmin, 2-methyloisoborneol [13].

The operations connected to processing and neutralisation of sludge are characterised by different levels of volatile odorous compounds emission [14]. One of the most frequently applied solutions, especially in bigger treatment plants, is methane fermentation with biogas recovery [15]. Due to its anaerobic character, this process generates significant emission of the odorous compounds, which is present in the post-fermentation sludge as well as in recovered biogas. The fermentation processes are usually carried out in closed chambers, which limits emission of odorants to the environment. The post-fermentation sludge can be rich in the odorous compounds, so it must be subjected to additional operations, such as dewatering, drying, biological stabilisation, before further management, for instance in agriculture [16]. Thermal processing of sludge gains has had increasing popularity as it allows for the transformation of organic compounds into stable forms, which are not hazardous to the environment [12].

Thus, it seems justified to conduct the research, which would describe the influence of selected volatile organic compounds released to ambient air on human health and related long-term hazards.

The magnitude of exposure risk for a wastewater treatment plant's employees depends on many factors, such as the size of the plant, amount and character of sewage entering the plant or employed technological solutions, including proper operation of the plant [17,18]. One of the most common tools used to evaluate the impact of a hazard on human health is risk assessment [19]. This technique allows for the identification of specific environmental problems and development of appropriate management strategies related to some hazardous chemicals, which can have a negative effect on both abiotic and biotic parts of the environment. Qualitative analysis of human health risks assumes that chemicals are distinguished between two categories: carcinogenic and non-carcinogenic, based on their abilities to induce some adverse health effects depending on the threshold level. In the literature, there are many examples of application of this approach to evaluate health risk of VOCs emitted from landfills and composting plants [17,20,21].

One of the main international organisations dealing with the classification of carcinogenic chemical factors is the International Agency for Research on Cancer (IARC). Its aim is the investigation of the contribution and human health risk-related properties of various factors, which could be present at the workplace and in the natural environment. The results of activity of particular working groups of the IARC are successive volumes of the contribution IARC *Monographs on the Evaluation of Carcinogenic Risks to Humans*, which contain the information on human health risk imposed by particular chemical compounds. Five categories of carcinogenic factors have been determined based on a number of criteria adopted by the IARC:

- Group 1—factor or set of factors carcinogenic to people;
- Group 2A—factor or set of factors, which is probably carcinogenic to people;
- Group 2B—factor or set of factors, which is presumably carcinogenic to people;
- Group 3—factor or set of factors, which cannot be classified as carcinogenic to people;

- Group 4—factor or set of factors, which are probably non-carcinogenic to people.

Despite numerous legal regulations introduced in many countries all over the world by the organisations such as the IARC, it is not a common practice to evaluate health risk connected with the volatile organic compounds generated during wastewater treatment plant operation. According to the authors, such evaluation should additionally take into account the determination of odour nuisance magnitude connected with sewage and sludge processing. Odour concentration can be supporting information about gaseous mixtures of VOCs. The presence of an unpleasant smell in any place is a form of indication, which can inform us about some human health risks [22]. Integrated risk assessment on the olfactory characterisation and human health effects of volatile compounds emissions from different processing units in WWTP have not been well studied. The investigations presented below concern the health hazard of wastewater treatment plant workers exposed to VOCs during working hours.

Based on the guidelines proposed by the US Environmental Protection Agency [23] and the classification of potentially carcinogenic compounds implemented by the IARC, this paper presents health risk parameters of cancer risk (CR) and hazard index (HI) determined for 5 selected compounds, which have been found to impose carcinogenic risks, and for 24 selected compounds, which have been found to impose non-carcinogenic risks. The investigations were performed using the instrumental and sensory methods in 4 main processing units of a wastewater treatment plant during spring and summer seasons in two consecutive years: 2017 and 2018. Evaluation of the CR and HI parameters was conducted according to the methodology proposed by the US EPA and the classification introduced by the working groups of the IARC [19] for the compounds identified using the GCxGC-TOF-MS technique, comparing the obtained spectra with the NIST spectra library and with the spectra of reference substances. The aim of the investigation is the determination of the wastewater treatment plant workers health risk due to carcinogenic and non-carcinogenic compounds as well as the health hazard connected with odour nuisance. According to the authors, it is one of the first attempts at simultaneous evaluation of carcinogenic and non-carcinogenic risks associated with emission of volatile odorous compounds released at different stages of wastewater treatment plant operation and determination of odour concentration levels. To our best knowledge, this type of investigation has not been performed so far regarding simultaneous utilisation of instrumental and sensory tools for health risk evaluation associated with the operation of wastewater treatment plants.

2. Materials and Methods

2.1. Sampling Site and Air Sampling Methods

A municipal wastewater treatment plant, located in the northern part of Poland, was selected for investigation. This object is one of the northernmost treatment plants in Poland. It is located close to the seaside, which is a popular tourist attraction. This treatment plant is a mechanical–biological WWTP with anaerobic fermentation of sludge, conducted with biogas recovery and its utilisation in a cogeneration process. Solid waste after mechanical treatment, such as sand and screenings, as well as post-fermentation sludge are subjected to composting processes. Table 1 presents the most important information concerning the amount of wastewater and sludge generated during the investigation period.

Table 1. Information about the amount of processed wastewater and sludge during the investigation period.

WWTPs Characteristics	2017	2018
Amount of wastewater supplied to the WWTP (m^3/day)	14,500	15,200
Amount of wastewater discharged from the WWTP (m^3/day)	8479	9360
Amount of generated sludge (t/year)	7207	8076

Air samples from the WWTP units were collected in spring and summer of 2017 and 2018. The spring period was from mid-March until mid-June, whereas the summer period started in mid-June and finished in mid-September. To characterise volatile organic compounds in various processing units, the air samples were collected at four different functional locations of the WWTP, presented in Figure 1: hall of mechanical treatment (HMT), biological reactors area (BRA), sludge composting piles (SCP) and solid waste composting piles (SWCP) from mechanical treatment section. Based on the literature, at these places odorous VOCs can be most significant, from a health risk standpoint. Air sampling was performed between 08:00 and 12:00 or between 13:00 and 15:00, i.e., in working hours, to ensure that the samples represented the air the WWTP employees would have inhaled. However, air disturbances caused by the employees were avoided. From each measurement location, a total of 36 air samples were taken (3 samples during every week). Hence, 144 samples were taken for each sampling campaign, leading to a total of 288 samples in spring and summer of 2017 and 288 samples in spring and summer of 2018.

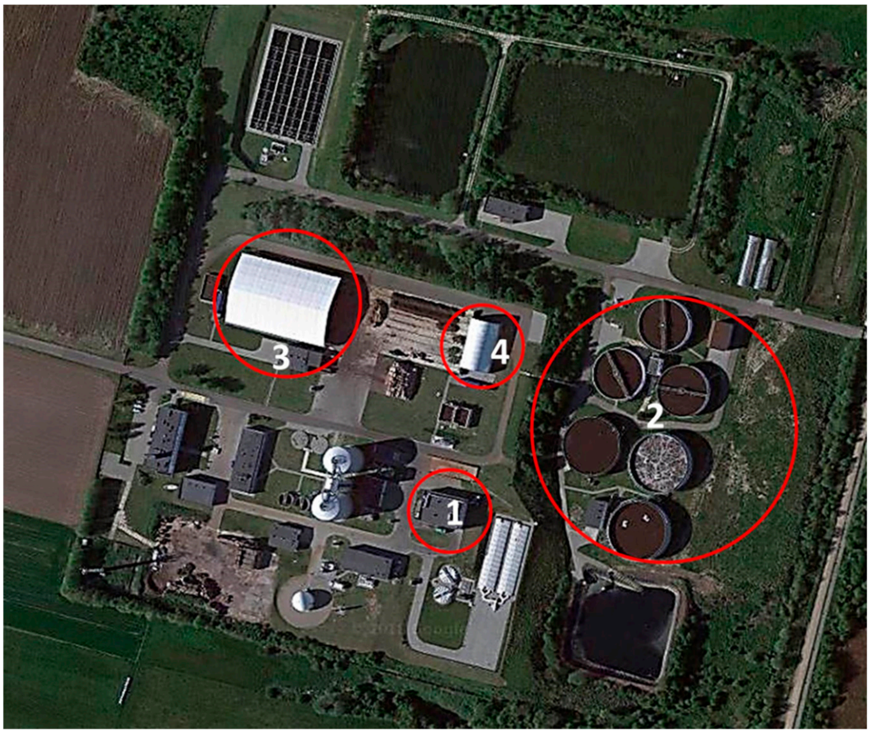

Figure 1. Measurement locations at WWTP; 1—hall of mechanical treatment (HMT), 2—biological reactors area (BRA), 3—sludge composting piles (SCP), 4—solid waste composting piles (SWCP).

At each measurement location, volatile compounds were adsorbed on a glass tube containing poly(2,6-diphenyl-p-phenylene oxide) known by its trademark Tenax TA, using a Gas Sampling System (GSS, GERSTEL, Germany). Analytes adsorption on the sorbent bed is caused by flow of air containing measured compounds. In this way, it is possible to collect the substances present in gas medium, for example in ambient air. In order to purify the sorbent from impurities left over from the previous analysis, each sorbent tube was thermally desorbed at 280 °C for 3 h, using high purity nitrogen. During each measurement series, the air stream was passed through the glass tube at the volumetric flow rate 75 mL/min for 15 min. After sampling, the sorbent tubes were stored in a sealed package at about 4 °C, for no longer than 48 h.

2.2. Sensory Analysis

According to the European Standard (EN 13725:2003), dynamic olfactometry is the recommended method for determination of odour concentration. Application of a field olfactometer is advised in case of measurement of odour emission from diffusion sources or for periodical emission as well as low and fast-changing odour concentrations. Therefore, the *Nasal Ranger* field olfactometer was used in this research. This device allows for a sensory evaluation based on the proportion of odorous air and the air passed through a dedicated carbon filter attached to the olfactometer. Before the measurement series, a preliminary test of individual olfactory threshold, using aqueous solution of n-butanol (according to the standard procedure development by the St. Croix Sensory, Inc., Stillwater, MN, USA), was conducted. As a result, from a group of 25 volunteers, four panellists (2 females, 2 males, aged 26–30) were chosen to conduct field measurements. Each panellist, during the measurement series, conducted 3 evaluations in each location at 10-min intervals.

During the olfactometric analysis, "dilution to threshold ratio" (D/T) values, which show the ratio of the air stream that passed through the carbon filter (V_{clean}) to the odour-containing air stream (V_{crude}), were measured. Based on D/T values, odour concentration was calculated according to the following Equations (1)–(4) [24]:

$$Z_{YES} = \left(\frac{D}{T}\right)_{YES} + 1 \tag{1}$$

$$Z_{NO} = \left(\frac{D}{T}\right)_{NO} + 1 \tag{2}$$

$$Z_{ITE} = \sqrt{Z_{YES} \times Z_{NO}} \tag{3}$$

$$c_{od} = \sqrt[n]{\prod_{0}^{n} Z_{ITE}} \tag{4}$$

where: Z_{YES}—dilution corresponding to the D/T value at which the odour is first perceived; $(D/T)_{YES}$—olfactometer disc position at which the odour is first perceived, directly succeeding the position at which it is yet imperceptible; Z_{NO}—dilution corresponding to the D/T value at which the odour is not yet perceptible; $(D/T)_{NO}$—olfactometer disc position at which the odour is imperceptible, directly preceding the position at which it can be perceived; Z_{ITE}—individual olfactory threshold; c_{od}—odour concentration (ou/m^3).

2.3. Analytical Method

The air samples were analysed using a thermal desorption unit—two dimensional gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled with a time-of-flight mass spectrometer (LECO Corp., St. Joseph, MI, USA). The sampling tubes were thermally desorbed for 10 min at 300 °C with a flow of pure helium gas passing through, carrying the desorbed gases to a pre-concentration trap, thermally desorbed at 300 °C and then the gases were transferred to the GCxGC-TOF-MS. Two capillary columns were used for the analysis: the first—Equity 1 (30 m × 0.25 mm × 0.25 µm) from the Supelco (Bellefonte, PA, USA); the second column—SolGel-Wax (2 m × 0.1 mm × 0.1 µm) was purchased from the SGE Analytical Science (Austin, TX, USA). Separation of the sample components was performed using the following program for the primary oven: initial temperature 40 °C, kept for 1 min, ramped at 10 °C/min to 90 °C, ramped at 3 °C/min to 240 °C and held for 3 min; for the secondary oven: initial temperature 45 °C, kept for 1 min, ramped at 10 °C/min to 95 °C, ramped at 3 °C/min to 245 °C and held for 3 min. As a carrier gas, high purity hydrogen (N6.0 class) with the constant flow rate 1 mL/min was used. Temperature of the transfer line and the ion sources was 250 °C. The voltage of detector was set at 1600 V. The modulation time was 5 s. Ions in the m/z = 40–500 range were analysed. Data analysis from chromatographic separation was done using the algorithm for peak deconvolution implemented in the ChromaTOF software (LECO Corp., version 4.24, St. Joseph, MI, USA).

The first stage of instrumental investigations was qualitative analysis of the samples using the GCxGC-TOF-MS technique in order to identify the entire spectrum of the compounds present in ambient air at selected measurement sites. The obtained list of compounds was compared with the NIST spectra library and with the spectra of reference compounds in order to ensure unequivocal identification.

In this way 24 compounds were selected for further studies. The second stage of instrumental measurements was quantitative analysis of the compounds identified before. It was conducted with TD-GCxGC-TOF-MS. Quantitative determination involved an external reference method [25]. The curve was constructed based on certified references of measured substances, just as in the case of the acquisition of the qualitative spectra at the compounds identification stage. The conditions of chromatographic measurements were identical at both the qualitative and quantitative analyses stages. The third stage was analysis of data from the RAIS and IRIS libraries [23] in order to determine for which of these 24 compounds it would be possible to calculate the CR and HI parameters, which describe whether a given compound can contribute to carcinogenic and non-carcinogenic risks. CR values could be determined for 5 compounds; for the remaining compounds it was possible to evaluate the HI parameter, which means that regardless of their concentration they did not contribute to an increase in the carcinogenic risk (the CR parameter).

2.4. Human Health Risk Assessment

The health risks imposed by VOCs inhaled by the plant's staff were assessed according to the US Environmental Protection Agency [23]. The risk of carcinogenic and non-carcinogenic effects is affected by inhalation exposure to the odorous substances with toxicological parameters. The maximum exposure concentration for an individual volatile organic compound (EC_i) was calculated according to the Equation (5):

$$EC_i = \frac{c_i \times DET \times EF \times ED}{AT \times 365 \times 24} \tag{5}$$

where: c_i—emission concentration for each volatile organic compound (ug/m^3) determined with GCxGC-TOF-MS system, DET—daily exposure time (6 hours/day in this study), EF—exposure frequency (350 days/year in this study), ED—exposure duration (35 years in this study) and AT—average time (25 years for non-carcinogenic risks and 70 years for carcinogenic risks). According to the US EPA guidelines, in the case of carcinogenic risk AT = lifetime and 70 years were accepted, similar to the other papers concerning carcinogenic risk in the vicinity of municipal plants; in the case of non–carcinogenic risk AT = exposure duration and 25 years were accepted similarly to the other papers. This time period was estimated as an average working time of the employee having contact with the installations such as wastewater treatment plants. However, these US EPA guidelines emphasise that in many cases, determination of the exposure duration can be troublesome because workers of the plant and residents of the area neighbouring the emission sources are exposed at varying levels and to different extents.

For carcinogenic effects, the health risk was calculated as a cancer risk (CR) according to the Equation (6):

$$CR_i = EC_i \times IUR_i \tag{6}$$

where: IUR_i—inhalation unit risk value ((ug/m^3)$^{-1}$). For non—carcinogenic effects, the health risk is expressed as the hazard index (HI), calculated based on the Equation (7):

$$HI_i = \frac{EC_i}{RfC_i} \tag{7}$$

where: RfC—reference concentration (ug/m^3). Both IUR and RfC values were taken from IRIS (Integrated Risk Information System) and RAIS (Risk Assessment Information System) databases [26,27].

Additionally, the chemical substances identified with the GCxGC-TOF-MS apparatus were classified according to the categories adopted by the IARC, presented in Section 1.

3. Results and Discussion

3.1. Volatile Organic Compounds Emission in WWTP

The volatile organic compounds, identified in selected locations at the wastewater treatment plant, represented different classes, mainly alcohols, aldehydes, ketones, esters, aromatic hydrocarbons and volatile organosulphur compounds. They are the substances frequently encountered in a vicinity of municipal plants, such as landfills or wastewater treatment plants [28,29]. Table 2 presents the percentage contribution of the most important compound classes in particular measurement locations in the conducted studies in 2017–2018. It is clear that the contribution of compound classes varies depending on the character of operations performed in a given location. Organosulphur compounds (21.1%—summer seasons, 22.9%—spring seasons) and aromatic hydrocarbons (20.8%—summer seasons, 19.7%—spring seasons) dominate in the hall of mechanical treatment. This observation can be explained by the fact that raw sewage, not subjected to any previous treatment, is exceptionally rich in these compounds. The sewage from households as well as industrial plants introduces a large amount of the aforementioned compounds [30]. Aliphatic hydrocarbons (24.8%—summer seasons, 23.1%—spring seasons) dominate in the air samples from the biological reactors area. They are characterised by much lower odour nuisance than aromatic hydrocarbons or organosulphur compounds, which is reflected in lower values of olfactory threshold that can be found in the literature [31]. The second major group in this location is ketones, the olfactory properties of which are diversified. The remaining two locations were dominated by organosulphur compounds (SCP: 29.1%—summer seasons, 29.9%—spring seasons, SWCP: 31.4%—summer seasons, 30.8%—spring seasons). Even at very low concentrations, these compounds reveal a strong odour. Hence, perceived odour strength was the highest in these two locations.

Table 2. Average percentage contribution of chemical classes at each area in WWTP under investigation (HMT—hall of mechanical treatment, BRA—biological reactors area, SCP—sludge composting piles, SWCP—solid waste composting piles).

	Percentage Contribution of Chemical Classes (%)							
Chemical Classes	**HMT**		**BRA**		**SCP**		**SWCP**	
	Summer	**Spring**	**Summer**	**Spring**	**Summer**	**Spring**	**Summer**	**Spring**
Sulphur compounds	27.1 ± 1.6	22.9 ± 1.6	7.7 ± 0.3	7.9 ± 0.2	29.1 ± 1.3	29.9 ± 1.1	31.4 ± 1.4	30.8 ± 2.0
Aromatic hydrocarbons	20.8 ± 1.4	19.7 ± 1.3	11.9 ± 0.4	12.9 ± 0.5	16.7 ± 1.0	12.9 ± 0.6	13.8 ± 0.6	15.0 ± 0.5
Aldehydes	11.2 ± 0.7	8.6 ± 0.6	14.2 ± 0.6	11.4 ± 0.5	8.2 ± 0.4	10.1 ± 0.5	9.2 ± 0.2	7.4 ± 0.3
Ketones	6.3 ± 0.3	6.7 ± 0.2	20.2 ± 0.9	22.4 ± 0.3	8.1 ± 0.5	9.4 ± 0.4	11.4 ± 0.4	10.4 ± 0.6
Aliphatic hydrocarbons	11.6 ± 0.6	12.7 ± 0.6	24.8 ± 1.2	23.1 ± 0.5	14.7 ± 0.8	15.6 ± 0.7	8.8 ± 0.4	9.9 ± 0.7
Alcohols	13.8 ± 0.8	16.9 ± 0.9	15.4 ± 1.1	21.1 ± 0.9	12.8 ± 1.1	12.0 ± 0.7	19.1 ± 0.6	19.7 ± 0.9
Others	9.2 ± 0.5	12.5 ± 0.4	5.8 ± 0.7	1.2 ± 0.2	10.4 ± 0.6	10.1 ± 0.7	6.3 ± 0.7	6.8 ± 0.7

Table 3 gathers the main chemical compounds identified at the area of investigated wastewater treatment plant, together with their olfactory thresholds and information about odour profiles. Odour nuisance associated with the processes and the unit operations carried out in wastewater treatment plants results not only from the olfactory properties of particular compounds, but also from synergistic effects of the odorants. It significantly hinders evaluation of the influence of these compounds on biotic and abiotic environment. The chemical compounds identified in sewage treatment plants can originate from sewage, some of them can be produced during sewage transport to the plant or during sewage treatment in different conditions of temperature, humidity, pH or possible presence of biological material and chemicals. An important factor, influencing odorants generation, is also oxygen content during sewage and sludge treatment. Low oxygen content in the sewage inlet channels favours the production of a significant amount of organosulphur compounds and carbonyl compounds.

Table 3. Chemical compounds identified in this study (olfactory threshold values from [31]; n.d.—no data).

1RT (s)	2RT (s)	Name of Compounds	Similarity	Odour Descriptors	Olfactory Threshold (ppm)
380	2.18	n-pentane	932	mild, sweet, gasoline	1.4
410	1.98	n-hexane	895	mild, gasoline-like	1.5
530	2.01	n-heptane	938	decayed, cabbage	6.7×10^{-1}
935	2.06	n-nonane	802	sharp	2.2
465	2.17	benzene	886	gasoline-like	2.7
925	2.35	ethylbenzene	931	aromatic	1.7×10^{-1}
876	2.11	propyl benzene	910	n.d.	3.8×10^{-3}
640	2.30	toluene	873	paint, solvent	3.3×10^{-1}
895	2.39	o-xylene	872	sweet, rubber	3.8×10^{-1}
845	2.32	m-xylene	927	sweet	4.1×10^{-2}
910	2.49	p-xylene	907	sweet	5.8×10^{-2}
1135	2.42	1,3,5-trimethylbenzene	905	sweet, aromatic	1.7×10^{-1}
1210	2.11	o-cresol	913	phenol-like	2.8×10^{-4}
1214	1.99	m-cresol	955	sweet tarry, phenol-like	1.0×10^{-4}
1220	2.32	p-cresol	833	feces	5.4×10^{-5}
1090	1.58	phenol	935	sweet tarry, acrid, sweet	5.6×10^{-3}
330	2.09	acetone	922	sweet, solvent	4.2×10^{1}
485	2.11	methyl ethyl ketone	918	pleasant pungent	4.4×10^{-1}
547	2.63	methyl isobutyl ketone	938	pleasant, camphor	5.0×10^{-1}
622	1.89	2-hexanone	944	pungent, acetone-like	2.4×10^{-2}
695	2.30	heptanal	882	pungent, linen	1.8×10^{-4}
620	1.98	formaldehyde	916	pungent, irritating	5.0×10^{-1}
745	2.28	acetaldehyde	922	ethereal	1.5×10^{-3}
425	2.32	methyl tert-butyl ether	901	distinctive, anesthetic-like	n.d.

1RT—first retention time; 2RT—second retention time; similarity—fitting probability between the mass spectrum obtained via chromatographic analysis and the spectrum contained in the NIST 2011 spectra library. Application of this algorithm allows for identification of measured substances.

3.2. Human Health Risk Assessment

The CR values were calculated for 5 compounds: 2 aromatic hydrocarbons (benzene and ethylbenzene), 2 aldehydes (acetaldehyde and formaldehyde) and for methyl tert-butyl ether. The highest values were observed for formaldehyde. The US EPA acceptable CR values for individual substances is 1.0×10^{-6}. Based on literature, the CR values larger than 1.0×10^{-4} are considered to be "definite risks", the substances with CRs from 1.0×10^{-4} to 1.0×10^{-5}— "probable risks", the substances with CRs from 1.0×10^{-5} to 1.0×10^{-6}— "possible risks" and the substances with CRs lower than 1.0×10^{-6} are considered to be "negligible risks" [20]. In our study, all CR values for formaldehyde exceeded the acceptable carcinogenic risk level (for both spring and summer). For methyl tert-butyl ether, the CR values were significantly smaller than the acceptable carcinogenic risk level. In all cases, the CR values presented in Figure 2 were smaller than 1.0E-04 and, based on the CR values for individual compounds, health risk can be considered not higher than "probable risks", except for formaldehyde. Figure 2 presents the CR values obtained in the research during spring–summer of 2017–2018 with classification of the CR values according to previously cited literature.

All HI values were not higher than the acceptable risk level for individual compound (HI = 1) [32], which was presented in Figure 3. A comparison of the HI parameter reveals that, regardless of the measurement location, the highest values were obtained for three aldehydes: acetaldehyde, formaldehyde and heptanal In some papers on health risk assessment, the HI parameter above 0.5 indicates "probable risk" [16].

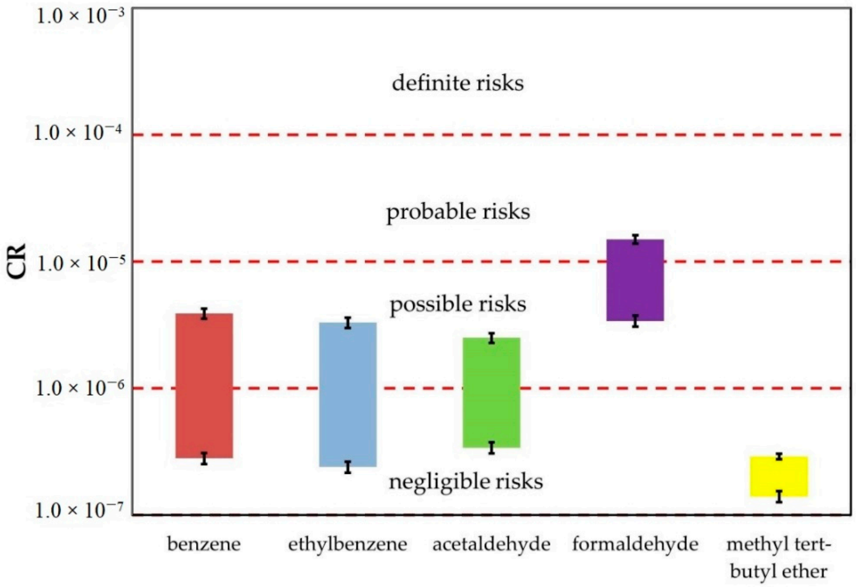

Figure 2. Ranges of cancer risk (CR) parameter determined based on investigations performed in both 2017 and 2018.

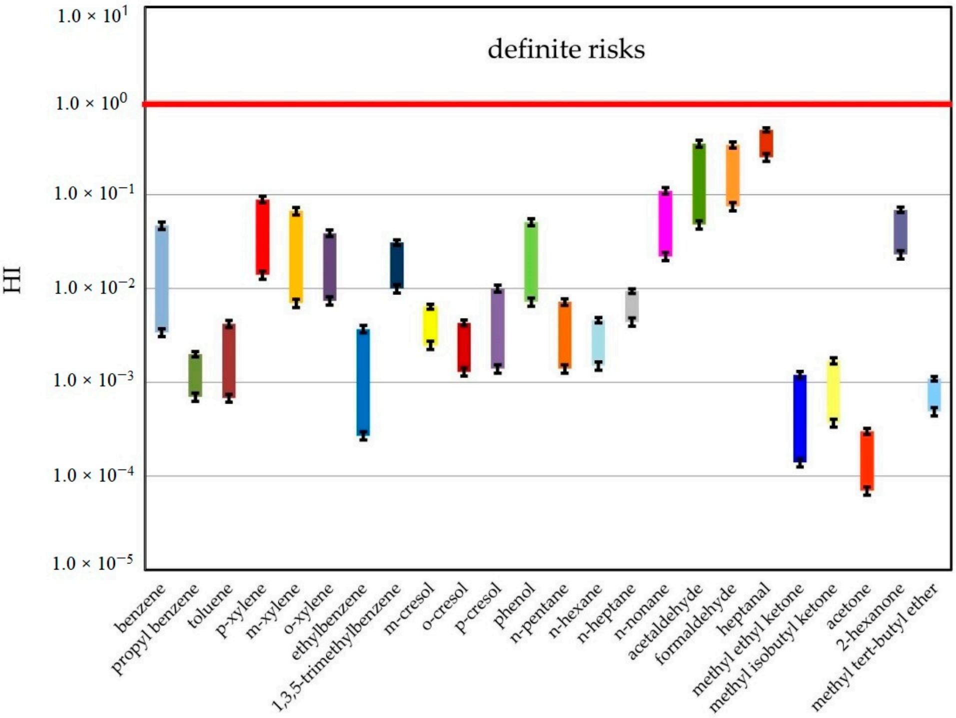

Figure 3. Ranges of hazard index (HI) parameter determined based on investigations performed in both 2017 and 2018.

Comparing our results with the ones obtained by other authors, Mustafa et al. [20] performed human health risk assessment related to the emission of volatile organic compounds generated during the unit operations connected with organic fraction degradation in one of the composting plants in China. The investigations were conducted in the winter and summer seasons, in order to evaluate differences in potential risk associated with the VOCs emission in different atmospheric conditions. The results revealed that the CR and HI parameters were below the acceptable limit ($CR < 1.0 \times 10^{-4}$ and $HI < 1$), except for those recorded for naphthalene in a biofilter ($CR = 1.1 \times 10^{-4}$, $HI = 3.07$ during the summer season). Marti et al. [33] also carried out a human health risk assessment, based on the

CR and HI parameters, for one of the landfills in Spain. In all cases, obtained values were within the acceptable limit. Durmusoglu et al. [19] conducted a health risk assessment with respect to aromatic compounds emission (benzene, toluene, ethylbenzene and xylenes) from a landfill in Turkey. Also in this case, the CR and HI parameters did not exceed the acceptable limits, which led the authors to a conclusion that the emission of the compounds from the BTEX group did not impose a health risk to the landfill's employees and to the residents of the neighbouring area. Table 4 presents a comparison of the CR and HI parameters obtained in this study with the results of other studies associated with emission of volatile compounds from various municipal facilities.

Table 4. Comparison of CR and HI values obtained in this study with other studies.

Study	CR	HI	Ref.
This study	1.4×10^{-7}–1.6×10^{-5}	7.0×10^{-5}–6.0×10^{-1}	-
BTEX emission in landfill environment	6.7×10^{-5}	1.4×10^{-2}–1.9×10^{-1}	[19]
VOCs emisssion in landfill area	3.5×10^{-11}–8.8×10^{-6}	2.6×10^{-4}–4.4×10^{-1}	[33]
	9.7×10^{-7}–1.3×10^{-4}	6.7×10^{-5}–7.3×10^{-1}	[32]
VOCs emission in composting plant	1.8×10^{-8}–1.1×10^{-4}	3.3×10^{-6}–0.3×10^{1}	[20]
	5.5×10^{-7}–1.9×10^{-4}	7.6×10^{-4}–4.0×10^{-1}	[21]

3.2.1. Comparison of Average Concentration of Particular Chemical Compounds with the Acceptable Concentrations Averaged over One Year Period

Based on the information contained in Table 5, which compares average concentrations during the entire measurement period for identified and quantitatively determined compounds belonging to the groups of carcinogenic and non-carcinogenic substances according to the US EPA with the acceptable concentration levels averaged over one calendar year (according to the Polish regulations), it can be noticed that the compounds from the carcinogenic group, such as formaldehyde and acetaldehyde, reveal possible a health risk (although average concentrations are higher than the acceptable level but the averaging period was limited only to the spring and summer of 2017 and 2018, which constitutes ca. 7% of the entire annual contribution). It was also observed that in the the entire measurement period, the compounds from the non-carcinogenic group according to the US EPA, including toluene, m-xylene, p-xylene, o-cresol, m-cresol, p-cresol, phenol, methyl isobutyl ketone, were characterised by average concentrations higher than the acceptable levels, regarding the same time span. Such a situation enforces the critical approach to the CR and HI parameters obtained for given chemical compounds. Moreover, a reliable health risk assessment of the wastewater treatment plant workers requires continuous monitoring of ambient air regarding particular chemical compounds emitted during sewage treatment, with special emphasis on variable emission levels of volatile organic compounds, depending on the season of the year as well as on such parameters as temperature, solar radiation or relative humidity. Continuous monitoring generates additional cost and quantitative determination of a big number of carcinogenic and non-carcinogenic compounds according to the US EPA, IARC or other international organisation guidelines is laborious. Thus, it seems that the summary CR and HI parameters would be better indicators than the CR and HI parameters determined for individual chemical compounds. It requires application of holistic analysis, which is provided by the olfactometric techniques. It seems that correlation of the results obtained with instrumental techniques with the olfactometric techniques results would allow for a fast evaluation of health risk level.

Table 5. Comparison of average concentration of identified compounds emitted during sewage treatment with acceptable concentration levels. Classification of these acompounds according to US EPA and International Agency for Research on Cancer (IARC).

Name of Compound	Average Concentration (μg/m^3)	Acceptable Concentration Averaged over One Calendar Year (μg/m^3)	Classification According to US EPA	Classification According to IARC
n-pentane	13.67	1000	HI	-
n-hexane	6.99	1000	HI	-
n-heptane	7.86	1000	HI	-
n-nonane	4.66	1000	HI	-
benzene	3.03	5	CR, HI	1
ethylbenzene	4.83	38	CR, HI	2B
propyl benzene	4.61	13	HI	-
toluene	40.49	10	HI	3
o-xylene	8.88	10	HI	3
m-xylene	12.65	10	HI	3
p-xylene	18.00	10	HI	3
1,3,5-trimethylbenzene	3.24	-	HI	-
o-cresol	6.11	1.6	HI	-
m-cresol	7.50	1.6	HI	-
p-cresol	10.04	1.6	HI	-
phenol	18.29	2.5	HI	3
acetone	17.07	30	HI	-
methyl ethyl ketone	8.29	26	HI	-
methyl isobutyl ketone	9.00	3.8	HI	2B
2-hexanone	4.16	-	HI	-
heptanal	3.40	-	HI	-
formaldehyde	6.00	4	CR, HI	1
acetaldehyde	5.63	2.5	CR, HI	2B
methyl tert-butyl ether	6.79	-	CR, HI	3

Analysing particular compounds with respect to a given classification elaborated by the IARC working group, it can be found that not all carcinogenic compounds according to the US EPA are also carcinogenic according to the IARC. Benzene and formaldehyde belong to the group 1—carcinogenic compunds, ethylbenzene and acetaldehyde are in the group 2B—compounds presumably carcinogenic to people, whereas methyl tert-butyl ether is in the group 3—compound not classified as carcinogenic to people. It should be noted that, apart from 5 compounds included in Figure 2, methyl isobutyl ketone also belongs to the group 2B (presumably carcinogenic to people) according to the IARC. Remaining identified compounds are classified into the group 3 or are not included in the IARC documents. This situation implies careful usage of the CR and HI parameters for particular chemical compounds. What is required is the knowledge not only of national acceptable levels but also of international regulations and guidelines concerning the health hazard of the workers exposed to the entire spectrum of compounds, including carcinogenic and non-carcinogenic ones.

3.3. Odour Concentration and Total Carcinogenic and Non-Carcinogenic Risk

The information presented in Sections 3.2 and 3.2.1 made the authors take a closer look at the problem of health risk of the workers exposed to inhalation of carcinogenic, non-carcinogenic as well as odour-nuisance generating compounds, which contribute to discomfort at wastewater treatment plants.

Conducted olfactory measurements made it possible to assess the odour concentrations in given locations, both during spring and summer seasons. These data together with summary values of the CR and HI parameters, determined separately for each measurement location and period, are presented in Figure 4a,b. The summary values of the CR and HI parameters were calculated as a sum of these parameters obtained for particular compounds. Utilisation of the summary values seems more convenient due to the fact that the people present in the given locations are exposed to simultaneous impact of volatile odorous compounds mixture, not to its particular components separately.

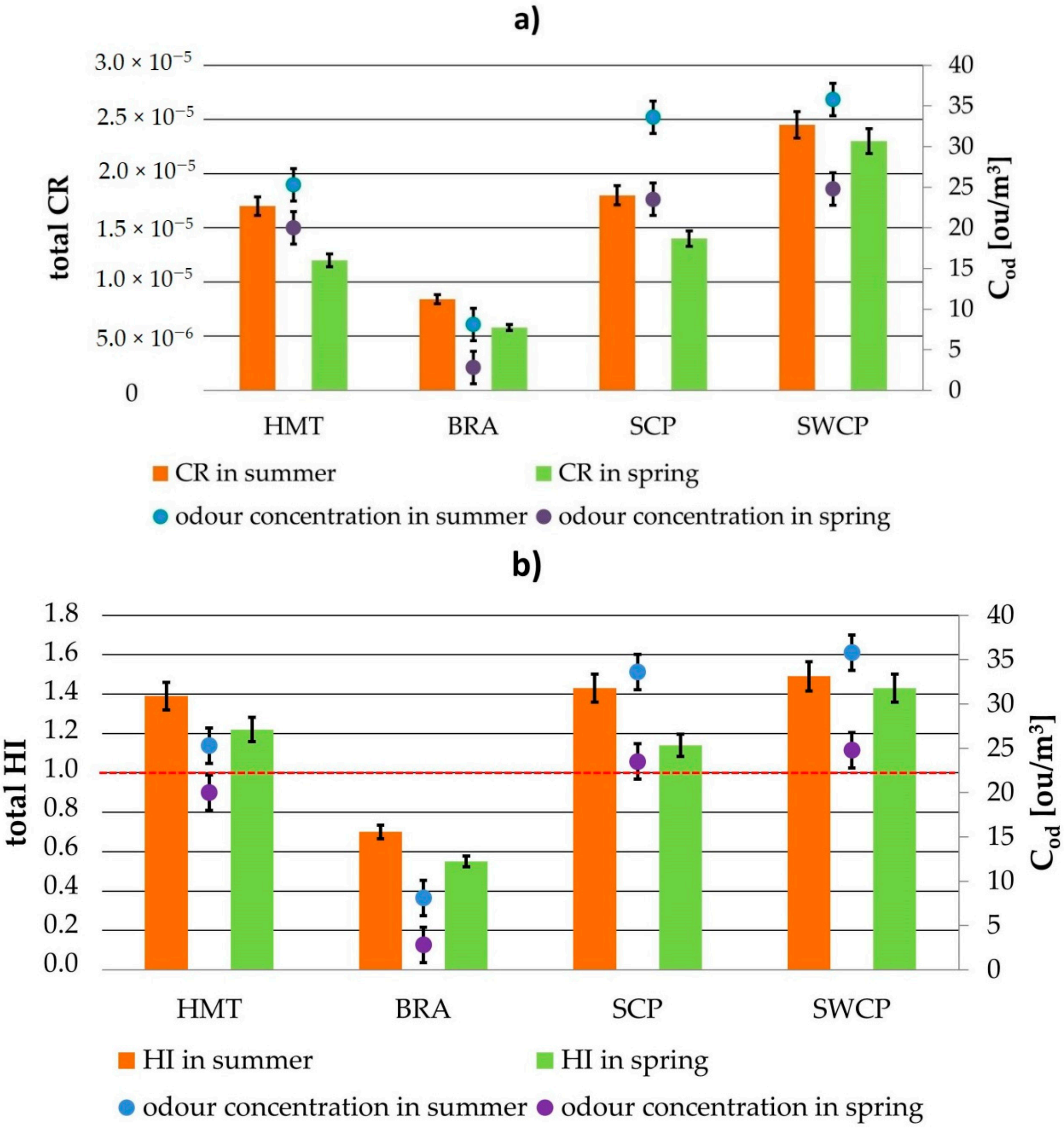

Figure 4. Total carcinogenic (**a**) and non-carcinogenic (**b**) risk in comparison to odour concentration values based on investigations performed in both 2017 and 2018.

Comparing the summary CR and HI values with the acceptable levels, it can be noticed that in the case of the carcinogenic risk, the summary CR values in each measurement location do not exceed the acceptable level (1.0×10^{-4}); for the summary HI values, HI < 1 only in case of the biological reactors area. In the remaining three locations, the acceptable level is exceeded to the value of ca. 1.6. For comparison, the investigations conducted in one of the composting plants in China revealed the summary HI parameter value in the range from 0.5 to 3.18, depending on location and season of the year [16]. Nevertheless, the results of our study show that special attention should be paid to the problem of volatile odorous compounds emission, particularly in the locations responsible for mechanical sewage treatment and composting process.

Figure 4a,b also contain the odour concentrations in given measurement locations. The highest c_{od} values were estimated for SWCP (37.2 ou/m^3 in the summer season of 2018, 24.9 ou/m^3 in the spring season of 2018). The lowest values occurred for the biological reactors area (8.11 ou/m^3 during the summer season of 2017 and 3.73 ou/m^3 during the spring season—both 2017 and 2018). It seems justified to conclude that odour concentrations are correlated with the values of CR and HI parameters; the higher the odour concentrations in a vicinity of the measurement sites, the higher the obtained values of the CR and HI parameters. Comparison of the results illustrated in Figure 4a shows that if odour concentration is above 10 ou/m^3, the CR parameter exceeds "probable risks" level (Figure 5a). Comparing the results presented in Figure 4b, it can also be qualitatively stated that if the odour concentration is above 15 ou/m^3, the HI parameter values will exceed the acceptable level (Figure 5b). In some cases such a situation would make it possible in the future to employ only olfactometric investigations to health risk assessment. Moreover, the olfactometric studies would lower the cost of continuous air quality monitoring in wastewater treatment plants. Obviously, it will require additional, many years' instrumental and olfactometric investigations to confirm this hypothesis.

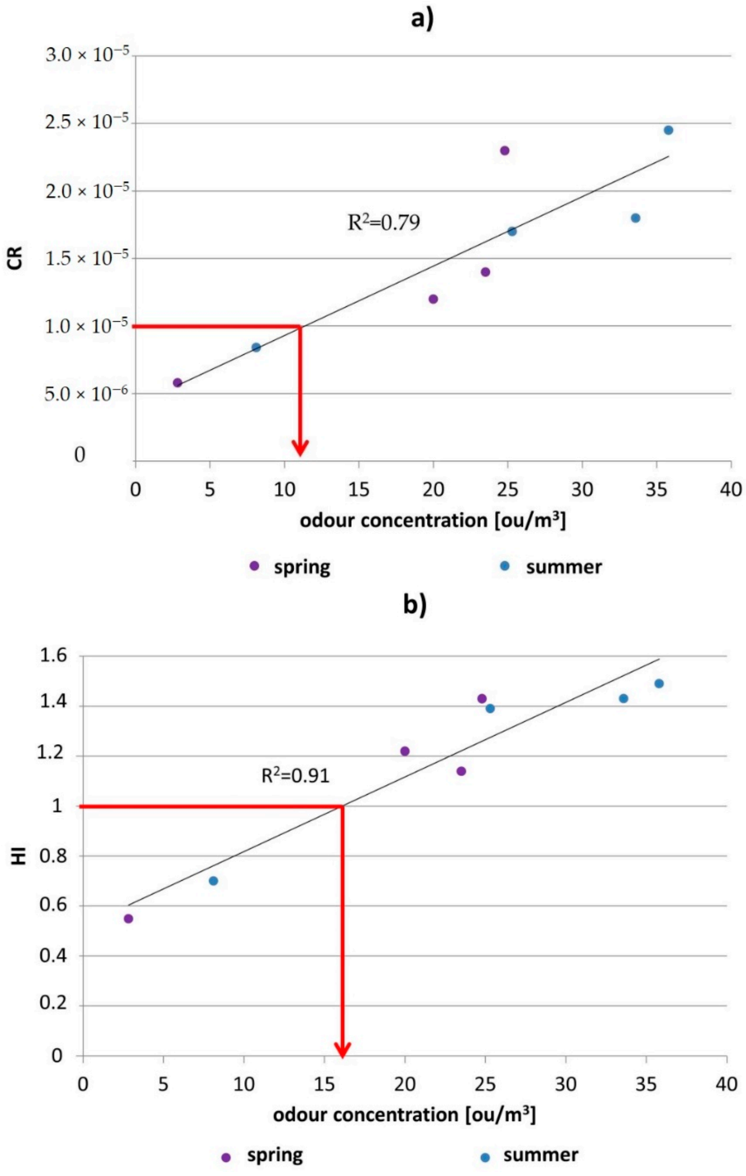

Figure 5. Dependence between CR and HI parameters and odour concentration: (**a**) CR, (**b**) HI.

The results of performed investigations indicate that the potential phenomenon of odour nuisance, due to the wastewater treatment plant operation, results mainly from increased emission of malodorous substances during mechanical sewage treatment as well as composting of sludge and solid waste from the mechanical treatment section. Similar observations are reported in the literature concerning the occurrence of odours in wastewater treatment plants. Lebrero et al. [30] showed that the biggest contribution to potential odour nuisance of a wastewater treatment plant originated from the operations of preliminary treatment and processing of sludge (thickening, dewatering, anaerobic fermentation).

Capelli et al. [34] compared odour concentration levels in 17 different wastewater treatment plants, taking into account 10 potential emission sources. Investigated treatment plants were divided into three groups regarding their size ("small"—treatment capacity within 10^3–10^4 m^3 per day, "medium"—within 10^4–10^5 m^3 per day and "large" within 10^5–10^6 m^3 per day). The highest odour concentrations were estimated in a stream of new-supplied sewage, during their mechanical treatment and during the operations connected with thickening and dewatering of sludge (odour concentrations amounted ca. 1000 ou_E/m^3). Based on the investigation, the authors concluded that the size of the plants did not have a significant impact on the magnitude of emission, both in particular sources as well as on the main source of malodorous compounds.

4. Conclusions

In this paper the authors presented a human health risk assessment for one of the wastewater treatment plants in northern Poland, according to the guidelines of the US EPA and the information contained in the IARC documents, taking into account the odour concentrations evaluated at the air samples collection sites. The investigations revealed that when analysing only the CR and HI parameters for particular compounds from the VOCs group, only in a minority of cases the substances present in selected measurement locations could influence the deterioration of the health of the plant's employees and the residents of the neighbouring areas. The highest health risk to the plant's workers originates from the substances, which are considered carcinogenic according to the IARC guidelines. Based on the CR parameters determined for these compounds following the US EPA methodology, it can be stated with certain probability that these substances, especially formaldehyde, may cause cancer disorders among the plant's employees. However, analysis of the summary values of the CR and HI parameters shows that, in selected locations, the HI parameter exceeds the accepted level, and the CR parameter is above the "probable risks" level. Moreover, it was observed that the odour concentrations were relatively well-correlated with the CR and HI parameters values; the odour concentrations above 10 ou/m^3 corresponded to the CR parameter at the level of 1.0×10^{-5} ($R^2 = 0.79$) and the odour concentartion above 15 ou/m^3 was connected with the HI parameter higher than 1 ($R^2 = 0.91$). Hypothetically, such a situation allows for the application of only olfactometric measurements to health risk assessment regarding carcinogenity. In the future, it would be enough to control the odour concentration level with the olfactomtric techniques and exceedence of accepted CR and HI parameters limits would be confirmed instrumentally. Such a situation would contribute to lower analysis cost and to a decrease in labour consumption. Obviously, confirmation of this hypothesis calls for further instrumental and olfactometric studies as well as toxicological examinations of the workers exposed to VOCs emission from the wastewater treatment plant.

The investigations showed that the health risk assessment of the wastweater treatment plant workers conducted with the instrumental and sensory methods was justified. Summary values of the CR and HI parameters indicate that new or improved solutions regarding the reduction of odour emission from the wastewater treatment plant should be implemented. Relatively high odour concentrations occuring in the volatile organic compounds emission sites also influence work discomfort in the plant.

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9.5. Załącznik nr 5

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Differences between selected volatile aromatic compound concentrations in sludge samples in various steps of wastewater treatment plant operations

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Dear Editor,
We have a pleasure to submit our paper entitled:

‘Differences between selected volatile aromatic compound concentrations in sludge samples in various steps of wastewater treatment plant operations'

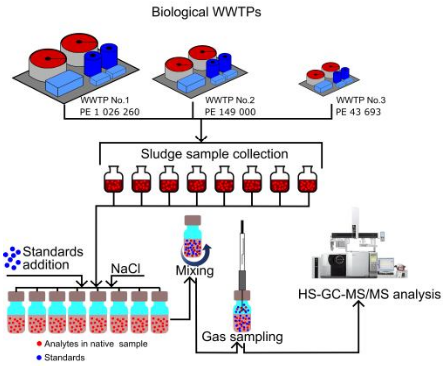
which we would like to publish in JOURNAL OF ENVIRONMENTAL MANAGEMENT.

The paper describes an application of the HS-GC-MS/MS technique to quantify the main volatile aromatic compounds present in various types of sewage sludge. Based on the obtained results, a relationship between the detected compounds and the type of sewage sludge within three analysed wastewater treatment plants have been find. In our opinion, information presented in this article can be useful to development of new solutions aimed at the limitation of emissions of volatile aromatic compounds formed during the operation of WWTPs.

We hope the information presented in the paper is a valuable scientific material for the potential readers.
We are looking forward to further stages of evaluation of the paper.

Kind regards
The authors

Graphical Abstracts



- A new method for determination of 7 compounds in sewage sludge was developed
- Relationship between the detected compounds and the type of sewage sludge was found
- Technological differences influenced the compounds' concentration in sludge samples
- Presented method found to be accurate and precise

ABSTRACT. Sewage sludge, one of the main wastes generated during wastewater treatment, constitutes an important source of emissions of volatile chemical compounds such as volatile aromatic compounds (VACs). These substances may undergo various changes as a result of operations and unit processes, which affects their concentrations in sewage sludge. An important factor determining the potential hazardousness of VOCs is the quality of wastewater delivered to wastewater treatment plants and the technical and equipment solutions applied to wastewater. In this study, a rapid and sensitive headspace gas chromatography method, coupled with tandem mass spectrometry (HS-GC-MS/MS) using the standard addition method, was developed for the determination of selected VACs in various sludge samples. The applicability of the method was verified by the analysis of sewage sludge samples collected at different stages from three wastewater treatment plants (WWTPs) located in Poland. This study attempted to assess the relationship between differences in the emissions of representative VACs and the given stage of the technological process within three analysed WWTPs. Toluene was detected with the highest frequency in analysed samples, at concentrations varying from 0.234±0.035 ng/g to 2830±320ng/g. The highest concentration levels were determined for p-cresol, with concentrations ranging from 440±56 ng/g of sludge (sludge from aerobic chamber, WWTP no.2) to 4770±690 ng/g of sludge(sludge from aerobic chamber, WWTP no.1), while the lowest concentration levels were observed for chlorobenzene ,with concentrations ranging from 0.1300±0.0030 ng/g of sludge(sludge from anaerobic chamber, WWTP no.2), to 0.2606±0.0046 ng/g of sludge (primary sludge, WWTP no.1). The repeatability of the method was better than 10%, with accuracy levels in the ranges 89%-108%.Wastewater treatment technologies and residual sludge management in the selected WWTPs influenced VACs emission. Furthermore, the diversity of the wastewater quality, depending on the catchment area, is also an important factor determining the differentiation in VACs emission. The microbial composition of raw wastewater highly influenced not only the treatment effectiveness of WWTPs but also the production of intermediate products, such as VACs, which may contribute to odor emissions.

KEYWORDS: gas chromatography – tandem mass spectrometry; headspace analysis; sludge; wastewater treatment plants; volatile aromatic compound

1. INTRODUCTION

Sewage sludge is one of the main types of solid waste generated during the treatment of municipal and industrial wastewater (Ruth M. Fisher et al., 2017). Despite the technological solutions implemented in wastewater treatment plants (WWTPs), this sludge remains a source of many harmful chemical substances, including volatile organic compounds (VOCs), which can be released into the environment, causing a negative impact (Cieślik et al., 2015; Gruchlik et al., 2013). The adverse effects of these compounds are associated with both the risk of pathogenic changes and psychosomatic symptoms associated with long-term residence in locations with high VOC concentration levels and include irritation, headache, anxiety, nausea, eye and throat irritation, shortness of breath, runny nose, sleep disturbance, insomnia, lack of appetite and irrational behaviour (Escalas et al., 2003). An odour nuisance problem is evidenced by an increasing number of complaints from residents of areas adjacent to WWTPs. Considering contemporary dynamic economic progress, it seems necessary to conduct research to monitor the presence of volatile organic compounds (Byliński et al., 2019; Gębicki et al., 2016).

Odour nuisance associated with sludge management results mainly from the emission of volatile sulfur compounds (VSCs). For this reason, most of the research on VOC emission from wastewater treatment plants focuses on VSCs (Fisher et al., 2018; R. M. Fisher et al., 2017; Lehtinen and Veijanen, 2011). The analysis of their transformation during sewage sludge processing is difficult to carry out, as some compounds (for example, mercaptans) are unstable (Chen et al., 2006). Therefore, the analysis of VOCs in sludge should include representatives of other compounds, e.g., volatile aromatic compounds (VACs). Even at low concentration levels, VACs contribute significantly to the formation of odour nuisance due to the relatively low values of their odour threshold. In addition, some of these compounds have carcinogenic properties, which significantly increases their potential negative impact on the environment (Fatone et al., 2011; Kacker et al., 2011). Therefore, it seems reasonable to monitor the transformation of VACs from emitters.

One of the basic analytical tools used to assess the emission of VOCs from sewage sludge is chromatographic techniques, including the gas chromatography - mass spectrometry (GC-MS) technique. This technique allows for both the identification and quantification of chemical substances present in various types of liquid and solid waste (including sewage sludge) generated by WWTPs. Methods based on GC-MS are characterized by a “green character” due to the relatively small amount of organic solvents used in common procedures. However, the GC-MS technique has some limitations related to its insufficient selectivity and sensitivity in the determination of some analytes (Woźniak et al., 2018). In recent years, interest in the gas chromatography technique coupled with tandem mass spectrometry (GC-MS/MS) has been increasing (Aszyk et al., 2018a; Zhang et al., 2015). This technique is characterized by a higher selectivity and sensitivity compared to the commonly used GC-MS technique (Aszyk et al., 2018b; Truta et al., 2016; Waraksa et al., 2018). Therefore, its potential application to assess VOCs released from sewage sludge is a subject of interest.

Most current procedures for analysis of VOCs in a gas sample use solid-phase microextraction (SPME) (Kotowska et al., 2012) or thermal desorption (TD) (Gallego et al., 2014) techniques. The advantage of these techniques is the possibility of enriching the analytes on the sorption fibre or bed used. However, a problem arises when selecting a sorbent with an affinity to a wide range of compounds with different chemical properties (e.g., polarity). It may be considered useful to develop new methods of gas sampling or to modify existing ones. The Environmental Protection Agency (EPA) adopted the static headspace (HS) technique to determine VACs present in environmental matrices (Hewitt, 1998; Voice and Kolb, 1994). By heating a small amount of a sample in a gas-tight vial, a mixture of volatile compounds will be transported from the sample into the headspace (Kolb, 2000). The compounds delivered into the headspace can be determined by GC combined with various detection systems, mainly GC-MS. It allows the introduction into the GC system of only volatile or semi-volatile compounds (Wardencki et al., 2007). The advantages of the HS technique are the relatively low cost of a single analysis and the lack of a large volume of organic solvent (Pascale et al., 2018). However, no validated HS-GC-MS/MS methods were found in the literature that allow for both qualitative and quantitative analysis of VACs present in sludge samples.

Despite the large amount of published data describing procedures for VOC analysis, to the best of the authors' knowledge, there are no scientific reports regarding the separation and quantification of VACs present in sludge samples with the aid of HS analysis combined with the GC-MS/MS technique. Therefore, the purpose of this study was an application of the HS-GC-MS/MS technique to quantify the main VACs present in various types of sewage sludge. An attempt was made to find a relationship between the detected compounds and the type of sewage sludge within three analysed wastewater treatment plants, including differences between sludge samples from the same steps in three different WWTPs and differences between sludge samples from various steps in each WWTP. The interpretation of the obtained results will allow for a better understanding of the differences in the emissions of representative VACs during technological processes occurring at a given stage of sewage sludge treatment.

2. MATERIALS AND METHODS

2.1. Wastewater treatment plant description and sample collection. Three municipal WWTPs with differences in terms of People Equivalent (PE) were selected for this investigation:

- WWTP no. 1 (PE 1 026 260),
- WWTP no. 2 (PE 149 000),
- WWTP no. 3 (PE 43 693).

Biological waste water treatment plants differ in terms of treatment technologies, especially in the case of excess sludge management. Differences between technologies result mainly from the size of the treatment plant, which is influenced *inter alia* by the PE and is associated with required limits/quality parameters for treated wastewater at the outflow ("Council Directive 91/271/EEC concerning urban waste-water treatment.," 1991). Selected WWTPs differ in size and applied technologies (Figure 1). The main difference between WWTP no. 2 and the remaining WWTPs is a lack of primary clarifier. In the case of WWTPs no. 1 and no. 2, flow biological reactors are applied. However, in WWTP no. 3, technology is based on a sequential biological reactor (SBR). In both WWTP no. 1 and no. 3, residual sludge treatment is based on anaerobic digestion, but in the case of WWTP no. 2, treatment is based on an aerobic digestion. The final residual sludge management in WWTP no. 1 is based on sludge incineration, and in WWTPs no. 2 and no. 3, sludge is intended for agricultural use (after prior stabilization).

<insert Figure 1>

Wastewater supplied to WWTPs has a typical municipal characteristic (please see Table 1); however, the COD/BOD ratio in WWTPs no. 1 and no. 3 testifies to the low biodegradability of wastewater (>2). Wastewater from WWTP no. 3 is characterized by a high N_{tot} concentration, which is caused by highly efficient dewatering of activated sludge (use of centrifuges instead of belt filter presses). Moreover, the characteristics of wastewater are influenced by the food industry (especially during the summer/tourist season).

<insert Table 1>

2.2 Reagents. All standards were supplied by Sigma-Aldrich (St. Louis, USA): benzene, toluene, p-xylene, ethylbenzene, chlorobenzene, p-cresol and skatole. Naphthalene-d8 was used as the internal standard (IS) and was purchased from Isotec/Sigma-Aldrich (St. Louis, USA). Methanol (MeOH, HPLC grade) was obtained from Merck (Darmstadt, Germany). Sodium chloride (NaCl) powder was obtained from POCH (Gliwice, Poland).

2.3. Preparation of standards. Stock solutions were prepared in MeOH by weighing an appropriate amount of the certified standard or by diluting the certified standard solution to 2 mg/mL. These solutions were used for the preparation of working standard solutions applied for quantification and validation of our methods. Stock solutions and working standard solutions were stored at −20°C until analysis. Fresh stock solutions were made each week.

2.4. Sample preparation and calibration. Sludge samples were mixed for 5 min using a magnetic stirrer. Dewatered sludge was mixed using a glass rod before conducting further steps. Sludge samples were weighed just before the chromatographic analysis in every instance. For every sample, six aliquots (approx. 5 g of sludge each) were weighed into a 15 mL headspace vial. Appropriate volumes of the standard working solutions were added to the five subsamples, while the sixth was used without standard addition. For each sample, the specific calibration curve range for each compound was applied, depending on the amount in the sample. The volumes of standard working solutions did not increase the sample volume by more than 5%. Subsequently, 2 g of NaCl was added, followed by the addition of 10 µL of 25 µg/mL IS. The IS concentration in each sample was kept at a concentration of 50 ng/g of sludge. Then, the headspace (HS) vial was sealed with a septum lined cap, and the samples were mixed for 30 seconds in order to homogenize the resulting mixture. Immediately after this operation, the samples were placed in an autosampler and analysed by HS-GC-MS/MS.

2.4. HS-GC-MS/MS conditions. The GC-MS/MS analyses were performed on a Shimadzu GC-2010 PLUS System (Kyoto, Japan) coupled with a Shimadzu TQ8050 triple quadrupole mass spectrometer (Kyoto, Japan). Separation of the analytes was performed on a Phenomenex ZB-WAX (30 m x 0.25 mm id, and 0.25 μm film thickness) capillary column. Helium (purity ≥ 99.999%) was applied as a carrier gas at a constant flow rate of 1 mL/min. The oven temperature was programmed from 40°C (held for 3 min), ramped to 90°C at 10°C/min, and then to 240°C (held for 2 min) at 30°C/min. The sludge samples were placed in 15 mL sealed vials, heated and agitated. The incubation temperature was kept at 70°C with an incubation time of 15 min. The injector port was kept at 240°C, in split mode (10:1), while the headspace syringe temperature was maintained at 85°C. The injection volume was 500 μL in the split injection mode. The temperatures of the ion source and MS interface were 220 and 235°C, respectively. The MS was operated in electron impact (EI) mode with an electron energy of 70 eV. Argon (purity ≥ 99.999%) was applied as the collision-induced dissociation (CID) gas with a scan range that covered 30-250 m/z. The instrument was operated in the multiple reaction monitoring mode (MRM). The monitored transitions and optimized collision energies (CEs) are listed in **Table S1**. The first ion transition was used for quantification, while the second was used as a qualifier ion. For each compound, the quantifier/qualifier ion ratio relative intensity was monitored.

2.5. Method validation procedures. The GC–MS/MS method was validated in terms of linearity, matrix effects, and accuracy, as well as intra- and inter-day precision according to the guidelines for analytical method validation (Chan et al., 2004; "Commision decision 2002/657/EC of 12 August 2002 implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results," 2002, "Guidance for Industry: Validation of Analytical Procedures and Methodology," 1996).

Each of the investigated samples is characterized by a different matrix composition (consistency, water content, homogeneity, density, etc.). Thus, part of the experiment was to investigate the influence of matrix effects on the accuracy by comparing the concentration of samples obtained with the application of the standard addition method with those obtained in pure water.

Calibration curves were constructed in three replicates based on the analysis of the analyte solutions in sludge by plotting the A/AIS ratios versus the analyte concentrations in sludge, expressed in ng/g of the sludge. The standard addition method was performed as follows: one unspiked sample aliquot of a real sample and five additional equal sample aliquots spiked with increasing levels of standard solutions were analysed. The linearity of the calibration curves was evaluated in the concentration range specific for each compound for a given sample (**see Table S2**). All samples were spiked with IS prior to the HS-GC-MS/MS analysis. Concentrations of the target analytes were estimated based on the extrapolation of a linear regression line on the concentration axis at zero signal.

The repeatability of the method was evaluated by a threefold analysis of two representative samples (sludge from anaerobic chamber, WWTP no. 1 and sludge from aerobic chamber in WWTP no. 2). The accuracy was estimated by spiking the sample with the appropriate amount of analytes. If an analyte was not present in a native sample, the low spiking level (0.1 ng/g of sludge) was applied. If standard reference samples were not available, the accuracy of the method was assessed through recovery experiments and expressed in terms of apparent percent recoveries. The data obtained for the accuracy evaluation were used for the intra-day precision. The inter-day precision of the developed method was evaluated by the analysis (n=3) of the two sludge samples spiked at defined spiking levels for the next three consecutive days. The precision of the method was expressed in terms of the coefficients of variation (CVs).

3. RESULTS AND DISCUSSION

3.1. Optimization of the HS extraction parameters. The incubation temperature is an important factor that has an influence on the sensitivity of volatile compounds by reducing their solubility and facilitating their transfer from the aqueous to the gas phase. In addition, high temperatures (>80°C) lead to water vapour formation in the sample HS, which may result in a decrease in response. Cavalcante et al. (Cavalcante et al., 2010) suggested that the optimal extraction temperature for BTEX should be kept at 70°C. In this study, the optimal responses for all analytes were observed at an incubation temperature of 70°C. At an incubation temperature of 70°C, a 15-min incubation time was sufficient to obtain high analyte response. Further increases in the incubation time had a negligible effect on the response of analytes. Additionally, the parameters of peak shape were within an acceptable range and a satisfying analyte response was obtained for an injection volume of 500 µL. Higher injection volumes resulted in the deterioration in peak shapes with a negligible increase in sensitivity. The influence of the salinity of samples on the HS procedure was investigated by comparing the response of analytes with different concentrations of NaCl added. The salinity of samples and ionic strength has an influence on the solubility of analytes and therefore analyte responses. A slight increase in analyte response was observed with an increasing NaCl concentration. The analytes' response was found to be the highest at a concentration of NaCl equal to 40% (w/w), and therefore, this amount was used in the samples.

3.2. Separation and detection condition optimization. In order to obtain high sensitivity and selectivity, chromatographic and mass spectrometry conditions were optimized. The temperature of the injection port, gradient temperature programme, carrier gas flow rate, source temperature, and the type of injection mode, split/splitless, were tested. The GC-MS was first operated in a full scan mode (35-200 m/z) to find the appropriate retention times for the analytes and to select ions for the MRM mode. For this purpose, a 500-µL aliquot of a mixture of the investigated analytes and the IS (50 µg/mL) in water was injected into the HS-GC-MS/MS system. The identification of analytes was confirmed with the use of the NIST library. The chromatogram obtained for the sample of sludge from the aerobic chamber spiked at a concentration level of 250 ng of toluene, 0.5 ng of benzene, p-xylene, chlorobenzene, and ethylbenzene, 2500 ng of p-cresol and 25 ng of skatole is presented in Figure 2.

<insert Figure 2>

Finally, the two selective and most abundant transitions were selected for quantification for most analytes. However, for benzene, for which two MS/MS transitions were not available, a pseudo-Multiple Reaction Monitoring (pseudo-MRM) was applied. In this mode, the precursor ion selected in the first quadrupole is subjected to zero collision energy and is applied as both a precursor and product ion and as a result a “pseudo” transition is created. It should be noted that only p-xylene, for which only the original quantitative standard was available in our laboratory, as a representative of xylenes isomers, was quantified. Another two isomers, ortho- and meta-xylene, were detected along with para-xylene. Notably, all isomers were well separated chromatographically, as presented in Figure 2. The identification of these two isomers of xylene was performed using the NIST library.

3.3. Method validation. Significant matrix effects affecting the accuracy were observed (data not shown), which may lead to under- and overestimation of the quantification results. Therefore, quantification was performed with the method of standard addition, due to the absence of a reference analyte-free sludge matrix.

The linearity of each calibration curve was assessed in concentration ranges specific for each analyte/sample. The coefficients of determination (r) were greater than 0.9990. The parameters of the calibration curves for detected substances are presented in Table S2.

The intra- and inter-day accuracy and precision data are presented in Table 2. Excellent percentage recoveries were obtained ranging from 89-108%, with acceptable variation better than 10%, both for intra-day and inter-day precision conditions. Thereby, the acceptance criteria (CV values were below 15%) for the analytical method validation was met (Chan et al., 2004; “Commision decision 2002/657/EC of 12 August 2002 implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results,” 2002, “Guidance for Industry: Validation of Analytical Procedures and Methodology,” 1996). The developed method is precise, accurate and suitable for sewage sludge sample analysis.

<insert Table 2>

3.4. Concentration of analytes in the investigated samples. The applicability of the elaborated method was verified by the analysis of 12 sewage sludge samples from three WWTPs collected at different stages of biological treatment. Each sample was analysed in triplicate. The results are expressed in ng of analyte per g of wet sludge. The concentration levels of target analytes in the investigated samples are summarised in **Table 3**.

<insert Table 3>

Compounds such as benzene, p-xylene, ethylbenzene and chlorobenzene were detected in low concentrations (range: 0.0396±0.0034-2.403±0.029 ng/g of sludge), while for toluene, skatole and p-cresol, high concentration levels were observed (range: 0.234±0.035-4770±690 ng/g of sludge). In only one sample (sludge from aerobic chamber from WWTP no. 1) were all investigated analytes quantified. Toluene was detected with the highest frequency in analysed samples in concentrations varying from 0.234±0.035 ng/g for primary sludge (WWTP no. 1) to 2830 ± 320 ng/g for dewatered sludge (WWTP no. 2). The highest concentration levels were determined for p-cresol with concentrations ranging from 440±56 ng/g of sludge (sludge from the aerobic chamber, WWTP no. 2) to 4770±690 ng/g of sludge (sludge from the aerobic chamber, WWTP no. 1), while the lowest concentration levels were observed for chlorobenzene with concentrations ranging from 0.1300±0.0030 ng/g of sludge (sludge from the anaerobic chamber, WWTP no. 2), to 0.2606±0.0046 ng/g of sludge (primary sludge, WWTP no. 1).

3.5. Interpretation of the obtained results. In general, all WWTPs may differ considerably in terms of the physical and chemical properties of treated sludge. As a consequence, various groups of VOCs may be emitted at any stage of wastewater treatment and excess sludge management (Lewkowska et al., 2016). Different chemical and biological processes and processing conditions such as pH, temperature, and retention time have an important effect on odour characteristics during the different stages of the treatment process. The formation of different substances (e.g., VSCs, VACs) may take place due to the different metabolic transformations of microorganisms occurring in the sludge during biological processes (Hort et al., 2009).

All studied compounds have been identified in primary sludge form in WWTP no. 1 apart from p-cresol and skatole. Nevertheless, the concentrations of these two compounds in sludge from the anaerobic and aerobic chambers differ significantly in comparison to other WWTPs (> 3000 ng/g and > 40 ng/g for p-cresol and skatole, respectively). The explanation is that the formation of these compounds is a result of the involvement of microorganisms in their release during biological wastewater treatment processes. Furthermore, the concentration of p-cresol and skatole is higher in the anaerobic than the aerobic chamber as a result of being easily released to the atmosphere when aeration is in use what is caused by the high dynamics of the involved processes. Similar to Chen et al. (Chen et al., 2006), the detected concentration of p-cresol may be explained due to the presence of tryptophan in sludge, which is one of the widespread protein amino acids derived from plant and animal cells. P-cresol may be formed from L-tyrosine under anaerobic conditions, especially in municipal sludge and in the petroleum contaminated medium (Mathus et al., 1995). Furthermore, the detected concentration of toluene in anaerobic and aerobic chambers (389±51 ng/g and 539±68 ng/g, respectively) is noteworthy. Industrial processes and household chemicals are suspected to be the origin of toluene. High concentrations of this compound in the stages of biological treatment in WWTP no. 1 are caused by the significant contribution of industrial wastewater in daily flow in comparison to other WWTPs (10-13%). The poor solubility of toluene in water may enhance its release into the atmosphere, especially during aeration processes (Lehtinen, 2012). In this study, an increased concentration of toluene in the aerobic chamber in comparison to the anaerobic chamber is observed (WWTP no. 1). Moreover, a rapid decrease in toluene emissions from digested sludge is noted (WWTP no. 1, Table 3) in comparison to the other studied samples. According to the results presented by Mrowiec et al. (Mrowiec et al., 2005) and Marczak et al. (Marczak et al., 2006), the toluene concentration increases during the first stage of the anaerobic digestion process (acidity phase) and decreases in the transition period (from the acidity phase to methanogenesis).

In WWTP no. 2, the highest emission of toluene is observed in the case of partially dewatered sludge. Toluene, due to its lipophilic properties, may adsorb onto the solid material of sludge and may be released during a change in temperature or pressure (Lehtinen, 2012). Hence, an increase in the toluene concentration after the dewatering process is observed (Table 3). However, lower values of p-cresol and skatole (667±47 and 440±56 ng/g, respectively) in comparison to WWTP no. 1 in the anaerobic and aerobic chambers are observed. In WWTP no. 2, the greater impact on wastewater quality may involve wastewater from septic tanks, which constituted about 3% and in WWTP no. 1 about 0.5% of daily flow. A common observation for both WWTPs is the fact that in both cases, the concentrations of p-cresol and skatole in the aerobic chamber were smaller than those observed for samples of sludge from the anaerobic chamber. At the same time, the concentration of these compounds in digested sludge samples was smaller than in the samples of sludge from the aerobic chamber. Regardless of the concentration of these compounds in the sludge delivered to the biological treatment stage, a significant reduction in their concentration may be noticed during the operations carried out both in these stages and in fermentation.

The concentrations of toluene, p-cresol and skatole in the primary sludge sample from WWTP no. 3 were the highest among the studied WWTPs. This may be related to tourism activity in this area during spring and summer, and hence, an increase in the supply of biological material containing both tryptophan and tyrosine (a potential source of skatole and p-cresol, respectively) is observed. In particular, the increased catering activities may cause the high delivery of the aforementioned aromatic amino acids. Moreover, WWTP no. 3 is located near the coast; therefore, the possibility of fish degradation impact is high. In addition, agricultural conferments (e.g., fish fat) in WWTP no. 3 were added during anaerobic digestion before the sampling campaign (according to personal commutation). The concentration levels of toluene in digested and dewatered sludge samples may be related to the methanogenesis stage of digestion and changes in physical conditions (temperature and pressure) (Lehtinen, 2012; Marczak et al., 2006; Mrowiec et al., 2005). Despite the three odour compounds mentioned above, the emission of other compounds is also observed. Furthermore, no compounds in waste activated sludge are detected. According to Zhang et al. (Zhang et al., 2013), these organic contaminants present in sludge might be oxidized after passing through activated sludge chambers and do not cause any additional odorous effect. This may happen primarily when adequate removal efficiency of nutrients and organic substances is obtained (see Table 1). A high content of skatole (Table 3) in primary sludge in WWTP no. 3 can be caused by the return of reject water obtained on the centrifuges, which are characterized by a higher efficiency of sludge dewatering compared to presses (which are used in WWTP No. 1).

The observed differences in the concentration levels of analytes may also be associated with the presence of a different level of unpleasant odour at the individual stages of sewage sludge treatment. Although it is widely recognized that the VSCs have the greatest impact on the degree of odour nuisance due to very low odour thresholds (OT), attention should be paid to the value of this parameter for some representatives of the compounds determined in this study. The OT value for toluene, p-cresol and skatole is 0.33 ppm v/v, 0.054 ppb v/v and 0.0056 ppb v/v, respectively (Nagata, 2003). These values, especially for p-cresol and skatole, are close to those observed for the most commonly determined volatile sulfur-based compounds released from sewage sludge. For this reason, these compounds can significantly affect the level of perceived fragrance, both due to the low value of the OT and the possibility of aroma effects with other fragrances released from the processed sewage sludge.

4. CONCLUSIONS

In this study, a rapid and sensitive HS-GC-MS/MS method for the identification and quantification of 7 volatile aromatic compounds in sludge samples has been presented. The presented method has been validated and was successfully applied for the determination of

VACs released from sewage sludge samples. In comparison to the commonly used methods of introducing volatile analytes into the chromatographic system such as LLE and SPME, the HS technique is characterized by the negligible consumption of organic solvents, which increases the green character of the presented method and the possibility of determination of a wide group of compounds. The main factor responsible for the effectiveness of identification with the use of this technique is the ability of HS to transfer analytes to the gas phase, which is commonly found in the case of VACs. The diversity in the composition of sewage sludge significantly impedes the interpretation of the reasons related to the varying levels of emission of volatile fragrance substances.

This work identifies only selected issues that significantly affect the variability of the formation of compounds potentially considered to be odorous. It would be beneficial to conduct similar studies, taking into account both the differences resulting from the location of the WWTPs, and hence the quality of wastewater, as well as the technological solutions adopted at the individual stages of wastewater and sewage sludge treatment. Research conducted in this area will certainly facilitate the refinement of existing solutions. It will also help in the development of new solutions aimed at the limitation of emissions of volatile aroma compounds, including those belonging to VACs, formed during the operation of WWTPs.

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None

ABBREVIATIONS

AN, anaerobic zone; AX, anoxic zone; BOD, biological oxygen demand; BTEX, benzene, toluene, ethylbenzene, xylenes; COD, chemical oxygen demand; CV, coefficient of variation;

GC-MS, gas chromatography – mass spectrometry; HS, headspace; HS-GC-MS/MS, headspace gas chromatography – tandem mass spectrometry; IS, internal standard; MRM, multiple reaction monitoring; N_{tot}, total nitrogen; OT, odor threshold; OX, oxic zone; P_{tot}, total phosphorus; PE, People Equivalent; Q_{av}, daily average wastewater flow rate; SPME, solid – phase microextraction; TD, thermal desorption; TSS, total suspended solids; VACs, volatile aromatic compounds; VOCs, volatile organic compounds; VSCs, volatile sulphur compounds; WWTPs, wastewater treatment plants;

SUPPORTING INFORMATION

Table S1-S2

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AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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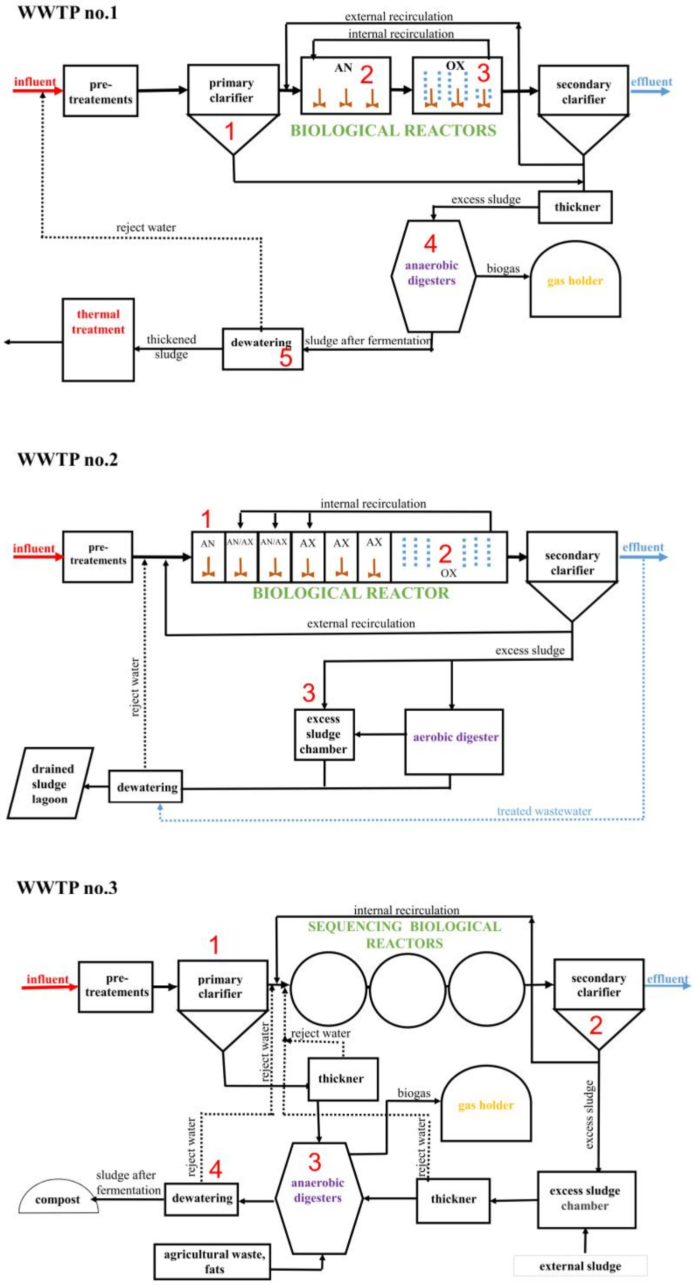


Figure 1. Technological lines of selected WWTPs and sampling points (AN – anaerobic zone, AX – anoxic zone, OX – oxic zone).

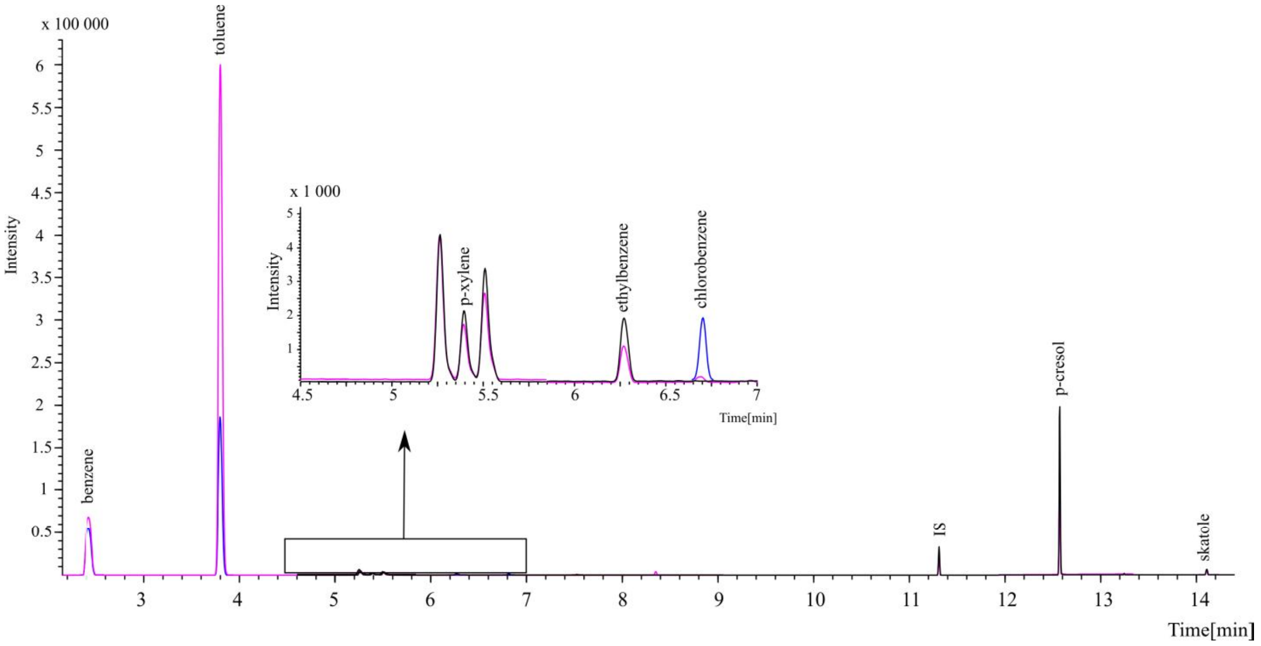


Figure 2. Example of chromatogram obtained for the sample of sludge from the aerobic chamber from WWTP no.1.

Table 1. Basic parameters of selected WWTPs during sampling campaign in 2018.

	PHYSICO-CHEMICAL PARAMETERS				
	TSS [mg/dm^3]	BOD$_5$ [mg O$_2$/dm^3]	COD [mg O$_2$/dm^3]	N$_{tot}$ [mg N/dm^3]	P$_{tot}$ [mg P/dm^3]
WWTP no. 1					
WWTP influent	304	243	626	41.3	5.89
WWTP effluent	8	4.9	43.4	8.4	1.24
WWTP no. 2					
WWTP influent	255	348	653	67.9	10.4
WWTP effluent	6.6	6.7	48.0	12.0	1.67
WWTP no. 3					
WWTP influent	124	320	955	122	9.6
WWTP effluent	8.0	8.0	43.5	8.1	0.46

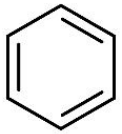
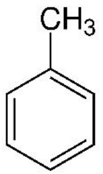
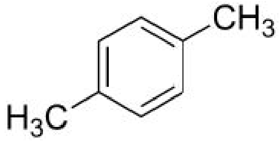
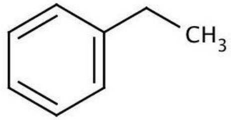
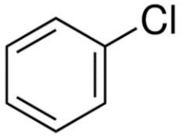
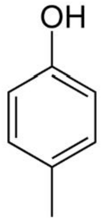
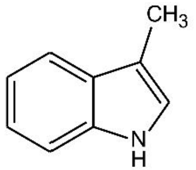
	TECHNICAL PARAMETERS	
	PE	Qav [m^3/d]
WWTP no. 1	1 026 260	173 176
WWTP no. 2	43 693	7 647
WWTP no. 3	149 000	6 164

Abbreviations: BOD-biological oxygen demand; COD-chemical oxygen demand; N$_{tot}$- total nitrogen; PE- population equivalent; P$_{tot}$ - total phosphorus; Q$_{av}$ – daily average wastewater flow rate; TSS- total suspended solids

Table 2. The intra- and inter-day accuracy and precision data.

Analyte	**Spiked amount [ng/g of sludge]**	**Intra-day accuracy and precision (n=3)**		**Inter-day accuracy and precision (n=3)**	
		Accuracy [%]	**CV [%]**	**Accuracy [%]**	**CV [%]**
Sludge from anaerobic chamber from WWTP no.1					
Benzene	0.1	91	8	97	4
Toluene	250	104	4	111	5
p-Xylene	0.1	95	3	98	7
Ethylbenzene	0.1	94	8	102	3
Chlorobenzene	0.1	91	2	101	4
p-Cresol	3500	103	8	107	9
Skatol	50	101	9	102	8
Sludge from aerobic chamber from WWTP no.2					
Benzene	0.1	108	3	105	2
Toluene	100	98	5	102	9
p-Xylene	0.1	89	8	99	10
Ethylbenzene	0.1	94	7	96	8
Chlorobenzene	0.1	95	4	94	5
p-Cresol	250	102	1	102	4
Skatol	25	107	2	93	3

Table 3. Average concentrations [ng/g of sludge ± SD (n=3)] of determined VACs in investigated sewage sludge samples.

SAMPLE		**CONCENTRATION OF ANALYTES ± STANDARD DEVIATIONS VALUES [ng/g wet of sludge]**						
		benzene	toluene	p-xylene	ethylbenzene	chlorobenzene	p-cresol	skatole
			 	 	 	 	 	
				WWTP no.1				
1	Primary sludge	0.546±0.033	0.234±0.035	0.264±0.010	0.2528±0.0083	0.2606±0.0046	n.d.	n.d.
2	Sludge from anaerobic chamber	0.0696±0.0041	389±51	0.1135±0.0040	n.d.	n.d.	4770±690	71.2±4.1
3	Sludge from aerobic chamber	1.051±0.092	539±68	0.506±0.032	1.155±0.064	0.253±0.029	3279±65	41.6±4.4
4	Digested sludge	n.d.	1.196±0.024	2.403±0.029	n.d.	n.d.	n.d.	n.d.
5	Dewatered sludge	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
				WWTP no. 2				
1	Sludge from	0.0396±0.0034	118.9±7.2	n.d.	n.d.	0.1300±0.0030	667±47	36.6±3.3

	anaerobic chamber							
2	Sludge from aerobic chamber	n.d.	8.31±0.75	n.d.	n.d.	0.206±0.011	440±56	n.d.
3	Dewatered sludge	1.31249±0.00048	2830±320	n.d.	n.d.	n.d.	n.d.	n.d.
WWTP no. 3								
1	Primary sludge	n.d.	1430±190	n.d.	n.d.	n.d.	1250±120	373±34
2	Waste activated sludge	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3	Digested sludge	n.d.	235±17	n.d.	n.d.	n.d.	n.d.	n.d.
4	Dewatered sludge	n.d.	301±24	n.d.	n.d.	n.d.	n.d.	n.d.

Table S1.

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Table S1. Monitored ion transitions and collision energies.

Lp.	Compound name	Retention time [min]	MRM transition, m/z (quantitative)	CE [V]	MRM transition, m/z (qualitative)	CE [V]	Ion ratio
1	Benzene	2.405	78.00>78.00	0	78.00>52.00	9	100/48
2	Toluene	3.784	91.00>65.10	12	92.00>65.10	27	100/27
3	p-Xylene	5.382	106.00>91.10	12	91.00>65.10	15	100/88
4	Ethylbenzene	6.256	106.00>91.10	12	91.00>65.10	15	100/77
5	Chlorobenzene	6.796	112.00>77.10	12	77.00>51.00	12	100/61
6	Naphthalene-d8	11.305	136.00>108.10	18	136.00>84.10	27	100/50
7	*p*-Cresol	12.563	107.00>77.10	12	107.00>79.10	6	100/35
8	Skatole	14.096	130.00>77.10	27	130.00>103.10	15	100/49

Table S2.

Table S2 Calibration data: slope and intercept with CVs values (n=3) for the standard addition method for analysed sludge samples. The calibration data were shown only for detected substances.

Sample type	Analyte	Calibration curve range (ng/g of sludge)	Slope [-]	SD [-]	CV [%]	Intercept [-]	SD [-]	CV [%]	r
WWTP no.1									
Primary sludge	**Benzene**	0.25-2.5	3.65	0.094	2.6	1.9903	0.0683	3.4	0.9939
	Toluene		0.1886	0.0022	1.1	0.0441	0.0061	13.9	0.9900
	p-Xylene		0.136	0.012	8.5	0.0359	0.0036	10.0	0.9951
	Ethylbenzene		0.0820	0.0036	4.3	0.0207	0.0012	5.7	0.9966
	Chlorobenzene		0.0819	0.0049	5.9	0.0214	0.0016	7.7	0.9937
Sludge from anaerobic chamber	**Benzene**	0.1-0.5	100.6	6.4	6.3	6.848	0.050	0.7	0.9992
	Toluene	50-500	0.1589	0.0054	3.4	66.1	1.2	1.9	0.9988
	p-Xylene	0.1-0.5	0.1135	0.0040	3.5	0.1135	0.0020	1.7	0.9902
	p-Cresol	1000-10000	0.00239	0.00011	4.4	17.07	0.88	5.1	0.9936
	Skatol	10-100	0.011154	0.000091	0.8	0.771	0.041	5.3	0.9979
Sludge from aerobic chamber	**Benzene**	0.5-2.5	11.14	0.97	8.7	11.652	0.081	0.7	0.9953
	Toluene	100-1000	0.3517	0.0025	0.7	176	11	6.0	0.9940
	p-Xylene	0.5-1.5	0.260	0.035	13.4	0.1306	0.0089	6.8	0.9982
	Ethylbenzene	0.250-2.5	0.0871	0.0021	2.4	0.1005	0.0032	3.2	0.9900
	Chlorobenzene	0.250-2.5	0.2631	0.0046	1.7	0.0621	0.0025	4.1	0.9932
	p-Cresol	1000-10000	0.001813	0.000018	1.0	6.012	0.091	1.5	0.9914
	Skatol	10-100	0.004314	0.000098	2.3	0.190381	0.000059	0.1	0.9939
Digested sludge	**Toluene**	0.250-1	1.573	0.044	2.8	1.881	0.049	2.6	0.9974
	p-Xylene	0.5-5	0.08836	0.00063	0.7	0.2123	0.0040	1.9	0.9979
Dewatered sludge	All analytes not detected								
WWTP no.2									
Sludge from aerobic chamber	**Toluene**	0.250-1	1.573	0.044	2.8	1.881	0.049	2.6	0.9974
	p-Xylene	0.5-5	0.08836	0.00063	0.7	0.2123	0.0040	1.9	0.9979
	Toluene	5-50	0.399	0.017	4.2	3.31	0.33	9.9	0.9900
	Chlorobenzene	0.25-2.5	1.37	0.10	7.6	0.2814	0.0088	3.1	0.9989

	p-Cresol	100-1000	0.00173	0.00019	10.9	0.76	0.12	15.5	0.9989
Sludge from anaerobic chamber	**Benzene**	0.1-0.5	100.6	6.4	6.3	6.848	0.050	0.7	0.9970
	Toluene	50-500	0.153	0.014	9.0	66.6	1.9	2.9	0.9951
	Chlorobenzene	0.25-1	2.9384	0.1067	3.6	0.3574	0.0242	6.8	0.9969
	p-Cresol	1000-10000	0.00239	0.00011	4.4	17.07	0.88	5.1	0.9931
	Skatol	10-100	0.011154	0.000091	0.8	0.771	0.041	5.3	0.9987
Partially dewatered sludge	**Benzene**	0.5-5	0.954	0.055	5.7	1.252	0.072	5.8	0.9938
	Toluene	250-2000	0.0742	0.0039	5.3	200	13	6.7	0.9900
WWTP no.3									
Primary sludge	**Toluene**	50-1000	0.407	0.058	14.4	573.8	4.4	0.8	0.9990
	p-Cresol	1000-1000	0.00404	0.00040	10.0	5.039	0.024	0.5	0.9989
	Skatol	50-1000	0.01991	0.00019	0.9	7.46	0.39	5.2	0.9900
Digested sludge	**Toluene**	100-1000	0.3095	0.0060	1.9	72.5	3.9	5.4	0.9951
Dewatered sludge	**Toluene**	50-1000	0.462	0.024	5.2	139.0	6.4	4.6	0.9949
Waste activated sludge	All analytes not detected								

9.6. Załącznik nr 6

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The use of artificial neural networks and decision trees to predict the degree of odor nuisance of post-digestion sludge in the sewage treatment plant process

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Abstract: The paper presents application of artificial neural networks and decision trees for prediction of odour properties of post-fermentation sludge from a biological-mechanical wastewater treatment plant. The input parameters were concentrations of popular compounds present in the sludge, such as toluene, p-xylene and p-cresol, and process parameters including concentration of volatile fatty acids, pH and alkalinity in the fermentation sludge. Presented analyses revealed that implementation of the artificial neural networks allowed prediction of the values of odour intensity and hedonic tone of the post-fermentation sludge at the level of 25% - mean absolute percentage error. Application of the decision tree made it possible to determine what input parameters the fermentation feed should have in order to arrive at the post-fermentation sludge with odour intensity <2 and hedonic tone >-1. It was shown that the aforementioned phenomenon was influenced by the following factors: concentration of p-xylene, pH, concentration of volatile fatty acids and concentration of p-cresol.

Keywords: sludge; wastewater treatment plant; HS-GC-MS/MS; odour prediction

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1. Introduction

Presence of odorous compounds in ambient air is a serious problem, especially for the residents of the areas directly adjacent to such municipal plants as wastewater treatment ones [1,2]. The odorous compounds can influence on deterioration of life quality causing the symptoms associated with long-term exposure including headache, nausea, problems with concentration, loss of appetite, stress, insomnia and discomfort [3]. Taking into account the unit processes in wastewater treatment plants, it was found that the operations connected with sludge processing constituted the main source of odorous substances emission [4,5]. Stuetz and Frechen, based on the investigations in the wastewater treatment plants in Germany and France, revealed that the operations connected with sludge thickening, dewatering and processing contributed to ca. 62% of the total emission of odorous compounds [6].

A regulation implemented in 2016, according to which disposal of municipal wastewater sludge on a landfill is banned, resulted in an increased interest in other, more pro-ecological methods of sludge management [7]. The most popular methods of sludge management include: use in agriculture for cultivation of non-consumption crops, reclamation and adjustment of soil to particular application, production of compost, use of sludge (after incineration) in building industry, production of adsorbents for industry and thermal utilization [8,9]. In order to provide safety, introduction of sludge to soil must be preceded by its dewatering, stabilization and composting. These operations are aimed at reduction of a risk of uncontrolled release of hazardous chemical substances to soil and ground water [10,11]. Utilization of sludge in building industry calls for its thermal treatment in order to produce ash. Depending on the other substrates admixed during building material formation process, it is possible to obtain a final product fulfilling required mechanical standards [12]. Thermal utilization of sludge is characterized by practically total mineralization of the chemical compounds present in the sludge. At high temperature (>700°C) organic substances are oxidized to simple inorganic compounds – mainly carbon dioxide and water. However, there is a risk of formation of the compounds more harmful for the environment, for example carbon monoxide, sulphur and nitrogen oxides [13]. A decrease in their emission during thermal processing can be achieved, among other things, via co-incineration of sludge with other energetic materials (coal, crude oil) [14].

Due to a complexity of wastewater sludge management problem, the number of respective legal acts is very big. One of the main related documents is the Directive of the European Parliament and Council 2008/98/WE of 19 November 2008, which contains the guidelines concerning environmental protection via prevention and reduction of negative effect connected with waste production. The Directive of the Council 86/278/EWG of 12 June 1986 implements the regulations related to usage of sludge in agriculture; the decree of the Minister of Development (Polish law) of 21 January 2016 defines the requirements concerning thermal management of waste; the Directive of the European Parliament and Council 2009/28/WE of 23 April 2009 describes required energy levels acquired from renewable energy sources, including biomass, which also engulfs wastewater sludge. The aforementioned legal acts do not pertain to admissible content of many hazardous chemical substances present in sludge as well as its further management. One of sparse examples indirectly referring to the discussed problem is a decree of the Minister of Environment (Polish law) of 9 September 2002 regarding soil quality standards, which mentions the values of admissible concentration of different pollutants, including aromatic hydrocarbons present in soil.

In case of the sludge management solutions described above, one of the main requirements is sludge stabilization. It is usually done in biological, chemical or thermal way [15]. One of the most frequently used forms of biological stabilization of sludge is anaerobic fermentation with simultaneous biogas recovery. This method gains popularity due to the fact that the energy generated during that process is regarded renewable one [16]. The sludge after anaerobic fermentation can still exhibit tendency to release chemical substances, including malodorous compounds [17]. One of the possibilities of reduction of the odorous substances present in the sludge can be control of this process in a way that maximizes evolution of VOCs and their transfer to biogas stream, which must be purified before further use.

Optimization of methane fermentation process by application of various model tools is a topic of interest for many scientists all over the world. One of the main models describing the anaerobic fermentation process is the ADM1 model elaborated by the International Water Association (IWA), which covers many physico-chemical and biochemical stages [18]. Bareha et al. investigated the possibilities of prediction of organic nitrogen compounds conversion during the methane fermentation process using fractionation methods [19]. Hu et al. made an attempt to elaborate a model methane fermentation system, which could be adopted to household wastewater treatment plants [20]. Ivanovs et al. presented the potentialities connected with model design of the methane fermentation process of fish waste, including biomethane generation [21]. These and other literature examples are characterized by relatively high complexity.

Among the solutions regarding modelling of sludge anaerobic fermentation, one can also find the investigations employing artificial neural networks. This tool allows very good reflection of complex dependences of a given process without taking into account detailed mechanisms of particular processes [22]. The artificial neural networks have already been used with the anaerobic fermentation process, for example for prediction of biogas production rate [23,24]. However, these papers did not take into account odour properties of the sludge before and after fermentation process.

The aim of presented investigation was verification of the possibility of artificial neural networks implementation for prediction of odour properties of the wastewater sludge subjected to anaerobic fermentation. The input data were: (i) concentrations of 3 odorous compounds from the volatile organic compounds group (toluene, p-xylene, p-cresol) present in the sludge, (ii) values of the parameters describing odour character of the investigated samples, namely odour intensity and hedonic tone, (iii) 3 most important parameters characterizing the methane fermentation process (volatile fatty acids, pH and alkalinity), the values of which differed during successive measurement cycles. Additionally, decision trees were used to determine what input parameters the fermentation feed should have in order to arrive at the post-fermentation sludge characterized by low odour intensity and hedonic quality. The instrumental and sensory techniques were employed in the measurements. The possibility of prediction of odour nuisance caused by post-fermentation sludge is a significant added value because it can define further sludge management in different fields of human activity.

2. Materials and Methods

2.1. Plants description and sampling methodology

Two wastewater treatment plants localized in Pomorskie voivodship (Poland) were selected to perform the investigations. Both plants employ mechanical-biological treatment with methane fermentation process and biogas recovery. The plant no. 1 treats bigger amount of sewage (55,000 m^3/day) than the plant no. 2 (10,000 m^3/day), which results in more sludge production (31 tons/day versus 6 tons/day, respectively).

In order to measure concentration of selected compounds from the volatile organic compounds group, the sludge samples were collected before and after the fermentation process. The samples were taken from 9 fermentation cycles. For each cycle, 12 sludge samples were collected prior to the fermentation and 12 samples were obtained following the fermentation in order to execute sensory measurements. Instrumental measurements involved 3 samples collected before the fermentation and 3 samples collected after the fermentation. The sludge was sampled into the 500mL glass bottles and transported to the laboratory. The investigations involved 135 samples of sludge collected before the fermentation and 135 sludge samples after the fermentation, which gives 270 samples from each treatment plant; the total of 540 samples of sludge were examined during the studies. The samples were stored at +4°C in sealed bottles between the sampling day and analysis day.

2.2. Chemicals, reagents and sample preparation

All chemical reagents used in this investigation were supplied by Sigma-Aldrich (St. Louis, USA): toluene, p-xylene and p-cresole. Methanol (HPLC grade) used as a solvent in stock solutions was obtained from Merck (Darmstadt, Germany); sodium chloride (NaCl) powder was obtained from POCH (Gliwice, Poland).

For each analysis, 5g of sludge were weighed into a 15 mL headspace vial. Subsequently, 2 g of NaCl were added for each sample. Then, the headspace (HS) vial was sealed with a septum lined cap, and the samples were mixed for 30 seconds in order to homogenize the mixture. After this operation, the samples were placed in an autosampler and analysed by HS-GC-MS/MS.

For quantification, stock solutions were prepared in MeOH by diluting the certified standard solution to 2 mg/mL. Stock solutions were stored at −20°C until analysis. Fresh stock solutions were made each week.

2.3. HS-GC-MS/MS conditions

For chromatographic separation, a Shimadzu GC-2010 PLUS system (Kyoto, Japan) equipped with an AOC- 20s autosampler was used. Separation of the analytes was performed on a Phenomenex ZB-WAX (30 m x 0.25 mm i.d., 0.25 μm film thickness) capillary column. As a carrier gas, helium (purity ≥ 99.999%) was applied, with a constant flow rate of 1 mL/min. The sludge samples were placed in 15mL sealed vials, heated and agitated. The incubation temperature was kept at 70°C with an incubation time of 15min. The injector port was kept at 240°C, in split mode (10:1), while the headspace syringe temperature was maintained at 85°C. The injection volume was 500 μL in the split injection mode. The oven temperature gradient program was as follows: 40°C (held for 3 min), ramp to 90°C at 10°C/min, then to 240°C (held for 2 min) at 30°C/min.

A Shimadzu TQ8050 triple quadrupole mass spectrometer equipped with a highly sensitive and stable ion source (Kyoto, Japan) was used in the study. The MS was operated in electron impact (EI) mode with an electron energy of 70 eV and temperatures of the ion source and MS interface were 220 and 235°C, respectively. Argon (purity ≥ 99.999%) was applied as the collision-induced dissociation (CID) gas with a scan range that covered 30-250 m/z. The instrument was operated in the multiple reaction monitoring mode (MRM).

2.4. Evaluation of odour of wastewater sludge samples

The samples of wastewater sludge were subjected to sensory analysis by a team of assessors trained in olfactometric analysis – 2 men and 2 women aged 25-30. The assessors evaluating odour of the samples by determination of odour intensity and hedonic tone fulfilled the requirements specified in the European standard PN-EN 13725:2007. For at least 30 minutes prior the evaluation, members of the team have not consumed any meals and they have not drunk anything, except water. Sensory analyses were performed in the laboratory. Odour intensity and hedonic tone were determined during the analyses according to the classification described in the German standard VDI 3940. Evaluation of odour intensity was carried out using 6-degree scale (particular intensity is assigned a value from 0 to 6 where 0 means no odour and 6 corresponds to extremely strong odour). Hedonic tone determination employed a scale, in which different odour categories are assigned with a value from -4 (extremely unpleasant odour), through 0 (neutral odour) to +4 (extremely pleasant odour). Each assessor was given a datasheet to put down the grades. The members of the team could not contact with each other in order to avoid exchange of information about the sensations associated with odour evaluations. The assessors were also obliged to take some breaks during the investigations to minimize a risk of olfactory adaptation. The results obtained during the sensory analyses were treated as the data to design a model taking into account odour properties of the sludge samples before and after the methane fermentation.

2.5. Data analysis

2.5.1. Artificial neural network

The artificial neural network was comprised of four layers:

- input layer (8 neurons),
- hidden layer (4 neurons),
- hidden layer (2 neurons),
- output layer (1 neuron).

Proposed network structure is dedicated to a problem of regression of a single property determined at the output of dataset. The neurons in a network's layer are connected with all neurons of the previous and following layers. Conical structure of the neural network was designed to strengthen generalization, which means better fitting of the network to new cases, unknown during a teaching process. Apart from the proposed network, the structures containing bigger number of neurons in each layer were also verified. However, they lost ability of generalization on the expense of better accuracy of regression for the cases defined in the teaching datasets. Mean absolute error (MAE) minimization was defined as a cost function during teaching process. Teaching and testing of the neural network employed k-fold technique. A dataset was divided into k equipotent datasets. Then teaching procedures were defined, where k-1 folds were used in neural network teaching process and remaining 1 fold was employed in testing process. The coefficient k=10 was adopted in the investigations. Moreover, in case of the data provided in k-1 folds 80% of it was attributed to neural network teaching and remaining 20% was used for model validation during teaching. 10 experiments were conducted for each model and obtained results were averaged. The k-fold technique minimizes the problem of data bias, which could influence on evaluation of designed models.

2.5.2. Decision trees algorithm

The algorithm of decision tree teaching is a non-arbitrary algorithm. The tree was taught by dividing a training set into subsets based on attribute value test. This process was repeated on every derivative subset in a recurrent way, named recurrent partitioning. Recursion is finished when a subset in the nod has the same all values of target variable or when division does not add any value to prediction. The main advantages of decision trees application are their non-parametric character as well as automatic identification of the most important variables by the algorithm and elimination of statistically insignificant variables. Moreover, mathematical transformation of one or more explanatory variables does not change the structure of a tree, which is altered only by the threshold values. A disadvantage is the fact that small modification of a training set (for example removal of a few observations) can result in a radical change of tree's structure. Additionally, in a single step the tree can divide the space only with respect to one variable. In other words, division lines are always perpendicular to division axis in variable space. All calculations were performed in RStudio 1.1.463 using the 'rpart' library.

3. Results

3.1. Concentration of investigated compounds in sludge samples

Application of headspace fraction analysis technique coupled with gas chromatography and tandem mass spectrometry allowed identification and quantitative measurement of concentration of 3 chemical compounds present in the investigated sludge samples. Literature survey shows that chosen compounds can be regarded the most frequently identified volatile aromatic compounds released from wastewater sludge, which have substantial influence on perceived odour connected with sludge processing [25–27]. Table 1 presents the concentration ranges of particular substances, including the sampling sites (before and after the fermentation process) and the treatment plant, from which the sample was collected.

Table 1. Concentration range of aromatic compounds in wastewater sludge determined before and after methane fermentation process using chromatographic technique.

measured compound	**concentration range [ng/g of sludge]**			
	WWTP no. 1		**WWTP no. 2**	
	sludge before fermentation	**sludge after fermentation**	**sludge before fermentation**	**sludge after fermentation**
toluene	1.3-7.0	4.1-12.0	7.2-16.4	15.0-25.3
p-xylene	8.0-18.3	4.3-10.0	10.2-20.9	3.2-15.0
p-cresole	12.9-19.0	3.2-9.9	7.2-12.9	5.1-10.9

Based on the data in Table 1, it can be seen that for the treatment plants no. 1 and 2 a content of toluene is higher in the sludge after fermentation than in the samples before that process. In case of the remaining two compounds their concentration is lower after the methane fermentation. It can be connected with decomposition of complex chemical compounds during the fermentation process.

Changes of toluene concentration in the sludge before and after fermentation are related to particular phases of the fermentation process. Earlier investigations reported that an increase in toluene concentration was observed during acetogenesis whereas methanogenesis was associated with a decrease in toluene content [28]. Table 2 shows the minimum, maximum and average values of three most important parameters characterizing the methane fermentation process: concentration of volatile fatty acids, pH and alkalinity defined as $CaCO_3$ content per one litre of fermentation mass for both wastewater treatment plants.

Table 2. Parameters describing operation of fermentation chamber.

parameter	**unit**	**WWTP no. 1**			**WWTP no.2**		
		minimum	**maximum**	**average**	**minimum**	**maximum**	**average**
VFAs	mg CH_3COOH/L	69.3	276.1	149.6	55.0	184.0	119.5
pH	-	6.1	7.7	6.9	6.1	7.5	6.9
alkalinity	mg $CaCO_3$/L	900.0	2575.0	1516.7	1274.0	3200.0	2060.4

Table 3 gathers average ranges of odour intensity and hedonic tone values determined for the wastewater sludge before and after the fermentation process including the wastewater treatment plant, from which the samples were collected.

Table 3. Average ranges of odour intensity and hedonic tone values determined by a team of assessors for wastewater sludge before and after fermentation process.

parameter	**WWTP no. 1**		**WWTP no. 2**	
	sludge before fermentation	**sludge after fermentation**	**sludge before fermentation**	**sludge after fermentation**
odour intensity	2.7-4.1	1.1-2.7	1.4-4.4	1.1-2.8
hedonic tone	-4.1 to -1.2	-2.6 to 0.3	-3.9 to -2.1	-2.9 to -1.4

After the methane fermentation odour intensity and hedonic tone values associated with the sludge decreased (regardless of the treatment plant). It is caused by the fact that some odorous compounds (especially volatile ones) moved into gas phase. Unfortunately, relatively big load of unpleasant odours is combined with the post-fermentation sludge. The value of odour intensity of the sludge oscillates between 1 and 3, which corresponds to clearly detectable odour intensity. In case of hedonic tone, this parameter for the post-fermentation sludge varies from -3 to 0, which means that the odour characteristics covers the range from very unpleasant to neutral. The possibility of prediction of odour intensity and hedonic tone values of the post-fermentation sludge by measurement of concentration of only 3 basic aromatic compounds (toluene, p-xylene, p-cresol) in fermentation feed and fundamental parameters of the fermentation process makes it possible to decide about further destination of the sludge. Prediction can be carried out with many methods but the authors employed artificial neural networks and decision trees. Fig. 1 depicts the plots presenting dependence between determined (evaluated) value and predicted value for a) odour intensity, b) concentration of toluene, c) concentration of p-xylene, d) concentration of p-cresole, e) hedonic tone, for the wastewater treatment plant no. 1. Fig. 2 shows analogous dependences but for the treatment plant no. 2.

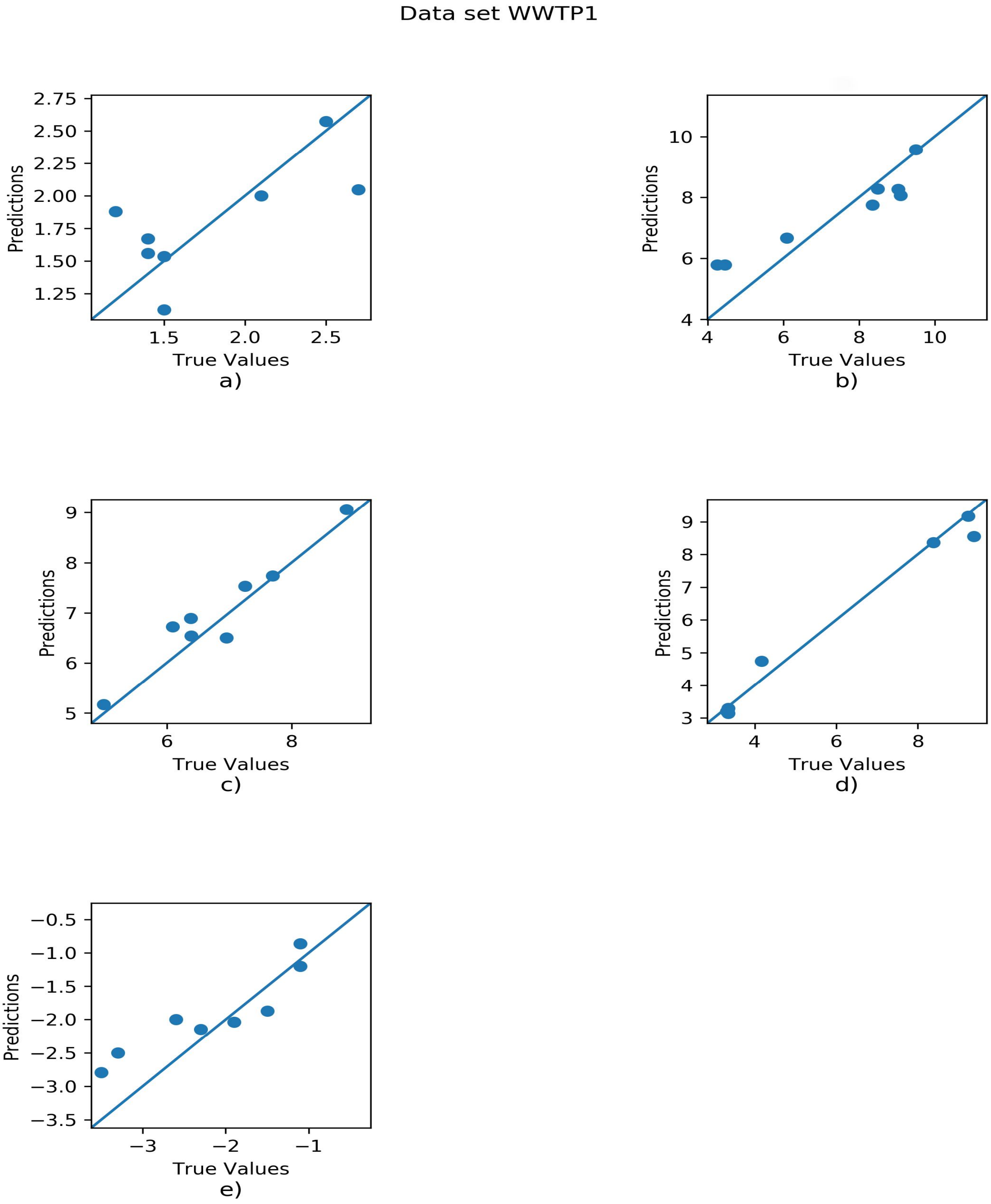

Figure 1. Dependence between determined (evaluated) value and predicted value for a) odour intensity, b) concentration of toluene, c) concentration of p-xylene, d) concentration of p-cresole, e) hedonic tone. Results obtained for wastewater treatment plant no. 1.

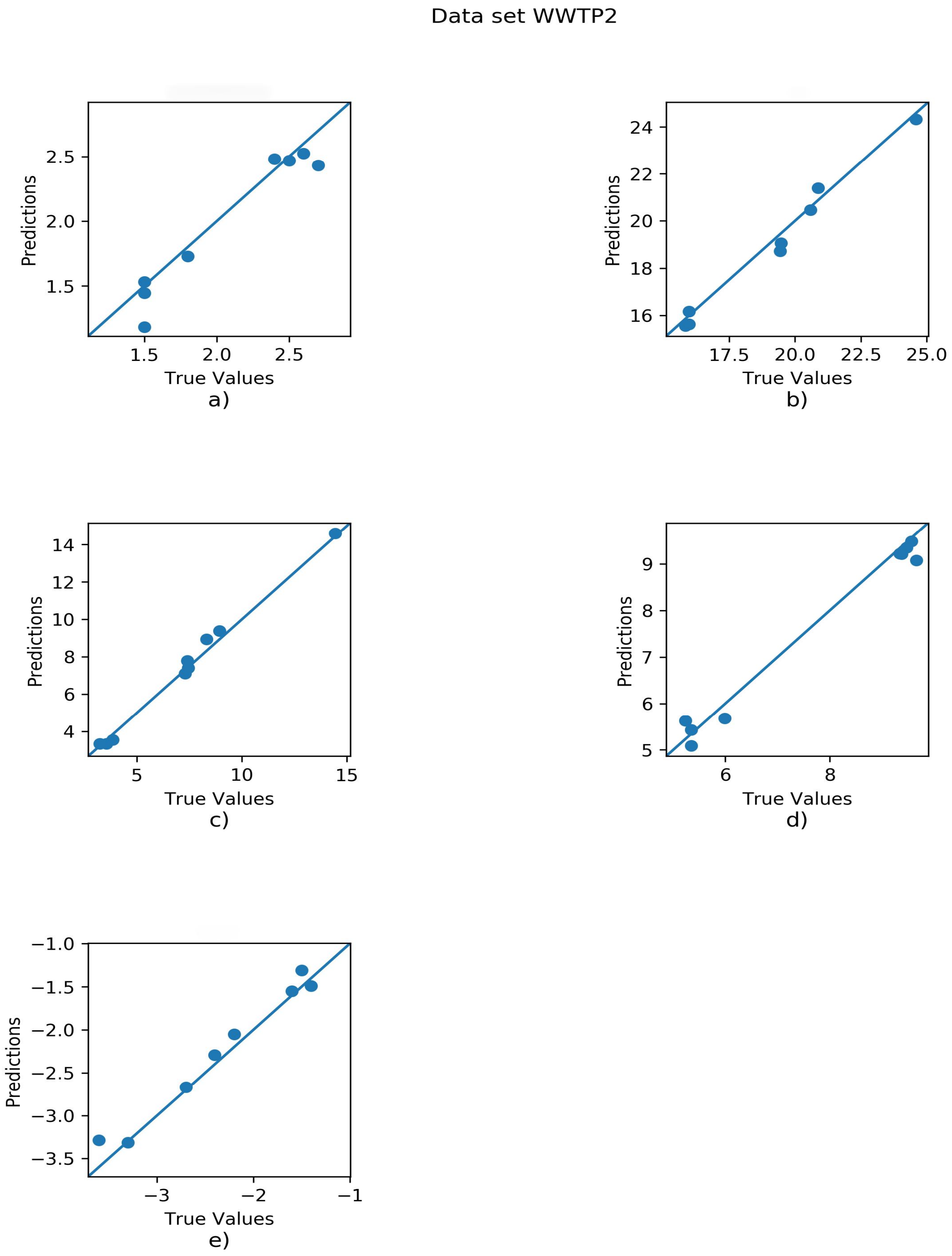

Figure 2. Dependence between determined (evaluated) value and predicted value for a) odour intensity, b) concentration of toluene, c) concentration of p-xylene, d) concentration of p-cresole, e) hedonic tone. Results obtained for wastewater treatment plant no. 2.

Table 4 presents the values of two metrics describing prediction level using artificial neural networks regarding odour intensity, concentration of toluene, concentration of p-xylene, concentration of p-cresole and hedonic tone of the post-fermentation sludge. Correctness of prediction was determined with MAE – mean absolute error and MAPE – mean absolute percentage error.

Table 4. Values of mean absolute error (MAE) and mean absolute percentage error (MAPE) for prediction of: odour intensity, concentration of toluene, concentration of p-xylene, concentration of p-cresole and hedonic tone of post-fermentation sludge for wastewater treatment plants no. 1 and no. 2.

parameter	**WWTP no. 1**		**WWTP no. 2**	
	MAE	**MAPE**	**MAE**	**MAPE**
odour intensity	0.57±0.30	28.99±13.15%	0.38±0.32	18.34±13.26%
concentration of toluene	1.95±0.87	26.11±10.77%	5.01±3.73	25.34±18.37%
concentration of p-xylene	0.95±0.62	12.93±7.95%	1.11±0.87	18.43±14.62%
concentration of p-cresole	1.43±0.64	21.43±9.56%	1.07±1.25	13.85±14.45%
hedonic tone	0.72±0.32	64.02±48.37%	0.57±0.42	26.43±19.62%

The information in Table 2 shows that the worst fitting is observed for odour intensity and hedonic tone (in case of the treatment plant no. 2 it is concentration of toluene not odour intensity that was characterized by the worst fitting). Such situation was expected because the odour mixture consisted of many components and our predictions were based on the information about concentration of only three components and 3 parameters of the fermentation process. Accepting this limitation, it can be stated that implementation of artificial neural networks provided satisfactory results as far as prediction of odour intensity and hedonic tone of the post-fermentation sludge is concerned. Average MAPE value for both predicted parameters was at the level of 25%, which suggests good fitting. Application of artificial neural networks and minimum input from process measurements allows satisfactory prediction of odour intensity and hedonic tone of the post-fermentation sludge. Such approach reduces time and cost connected with laboratory and olfactometric analyses, which require not only qualified personnel but also special laboratory fulfilling strictly defined rules concerning olfactory measurements. Routine measurements make it possible to assess odour nuisance with relatively good approximation via evaluation of two fundamental properties of odour – its intensity and hedonic tone. This knowledge helps to decide about further destination of the post-fermentation sludge; whether it can be used in agriculture, for cultivation of non-consumption crops, production of compost or directed to thermal utilization.

Fig. 3 illustrates a decision tree, which allows prediction of the process parameters of the fermentation feed in order to obtain the post-fermentation sludge characterized by odour intensity below 2 (weak) and hedonic tone above -1 (slightly unpleasant).

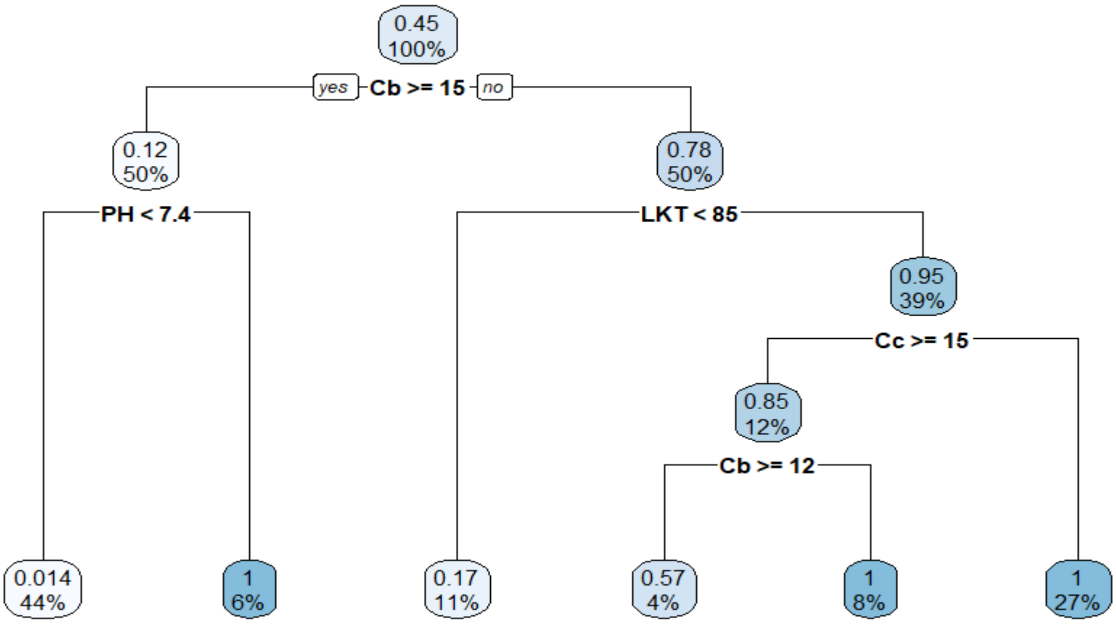

Figure 3. Decision tree defining process parameters of fermentation feed necessary to arrive at weak and slightly unpleasant odour nuisance of post-fermentation sludge.

Looking at the presented decision tree it can be noticed that if p-xylene concentration is higher than 15 ng/g of sludge and pH of sludge exceeds 7.4 then obtained post-fermentation sludge will be characterized by odour intensity <2 and hedonic tone >-1. When p-xylene concentration is lower than 15 ng/g of sludge, then odour intensity <2 and hedonic tone >-1 can be achieved if concentration of volatile fatty acids is above 85 and p-cresole concentration is below 15 ng/g of sludge or if concentration of volatile fatty acids is above 85, p-cresole concentration is above 15 and p-xylene concentration is below 12 ng/g of sludge. It is evident that in order to determine and predict odour intensity and hedonic tone of the post-fermentation sludge characterized by moderate odour nuisance, it is enough to know concentration of p-xylene, p-cresole, pH or concentration of volatile fatty acids. Obviously, the certainty level is limited to 67% (0.45*0.12 + 0.45*0.78*0.95 + 0.45*0.78*0.95*0.85).

Proper control of the process and selection of the fermentation feed allows obtaining the post-fermentation sludge with defined odour parameters. Implementation of artificial neural networks and decision trees, with simultaneous minimum measurement input (measurement of concentration of three basic aromatic hydrocarbons and three process parameters) give the possibility to predict odour intensity and hedonic tone of the post-fermentation sludge and what parameters the fermentation process should have in order to arrive at the post-fermentation sludge with defined odour intensity and hedonic tone values. Such approach results in reduction of process control cost and allows obtaining of the post-fermentation sludge characterized by defined parameters and ready for further processing.

5. Conclusions

The paper presents application of artificial neural networks and decision trees to prediction of odour properties of the post-fermentation sludge from two biological-mechanical treatment plants localized in the north of Poland. The input parameters were concentrations of popular compounds present in wastewater sludge: toluene, p-xylene and p-cresole. Additional parameters employed in the prediction process included concentration of volatile fatty acids, pH and alkalinity in the post-fermentation sludge. Performed analyses proved that implementation of the artificial neural network with the structure 8-4-2-1 allowed prediction of odour intensity and hedonic tone values of the post-fermentation sludge at the level of 25% in terms of mean absolute percentage error. Taking into account low number of the input parameters used for prediction of odour intensity and hedonic tone, the performed prediction can be regarded satisfactory, especially as the analysed odour mixture consisted of many components, which influenced on perceived odour intensity and hedonic tone of the post-fermentation sludge. Utilization of the decision tree made it possible to determine what input parameters the fermentation feed should have in order to obtain the post-fermentation sludge with odour intensity <2 and hedonic tone >-1. It was found that these parameters involved concentration of p-xylene, pH, concentration of volatile fatty acids and concentration of p-cresole.

The authors realise that presented studies should be continued to elaborate optimum process conditions and to determine the minimum number of measurements allowing fast process control aimed at evaluation of odour nuisance of the post-fermentation sludge. Nevertheless, it seems that presented results are promising and can contribute to effective management of the post-fermentation sludge in different fields of human activity.

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9.7. Załącznik nr 7

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