French agency for food, environmental and occupational health & safety

The Director General

Maisons-Alfort, 16 June 2011

OPINION
of the French Agency for Food, Environmental and Occupational Health & Safety

on risks from gas emissions by green algae to the health of local residents, walkers and workers

ANSES undertakes independent and pluralistic scientific expert assessments.

ANSES primarily ensures environmental, occupational and food safety and assesses potential health risks in these areas.

It also contributes to the protection of the health and welfare of animals, the protection of plant health and the evaluation of the nutritional characteristics of food.

It provides the competent authorities with all necessary information concerning these risks as well as the requisite expertise and scientific and technical support for drafting legislative and statutory provisions and implementing risk management strategies (Article L.1313-1 of the French Public Health Code).

Its opinions are made public.

On 23 February 2010, the Agency received a formal request from the Ministries for Ecology, Labour and Health for an Opinion on the risks from gas emissions by green algae to the health of local residents, walkers and workers.

1. BACKGROUND AND SUBJECT OF THE REQUEST

For several decades now, sections of the French coastline have been affected by "green tides". This was originally a small-scale phenomenon, but has increased considerably in recent years. Brittany is the most heavily affected region, but the Cotentin Peninsula and the Charente-Maritime *département* also suffer. These masses of green algae washed up on the beaches – apart from their negative impact on tourism – release significant amounts of gas as they decompose, particularly hydrogen sulfide (H_2S). Considering the known hazards of hydrogen sulfide, the threat of health problems and unpleasant odours must be considered, whether for the general population (local residents and people walking in the vicinity) or for those working by the shore (shellfish gathering, leisure activities, etc.). To overcome this pollution, the algae are removed from some beaches. Once collected, they are transported, transformed and processed in a variety of ways. All these activities can lead to the exposure of other population groups, and the workers in this sector, to emissions from decomposing algae.

The proliferation of green algae is mainly related to the high concentrations of nitrates in water, resulting from human activities (especially agriculture), and the particular shape of the coastline (a large number of bays). Several species of algae can be found in the deposits but the *Ulva* genus predominates because of the speed at which it proliferates in light when floating freely in Ulva belts close to the coast.

In an attempt to stem this phenomenon, the French government drew up a plan in February 2010 to fight green algae for the period 2010-2015. The goal is to manage the risks associated with the green algae and to implement measures from 2010-2011 to reduce nitrate emissions by at least 30 to 40% by 2015 in the eight "green algae" bays identified in the Master plan for water management and development (SDAGE) for the Loire-Bretagne watershed. The plan has three separate levels and involves:

- implementing preventive measures to stop nitrogen emissions from running into the sea (through improved treatment of effluents and waste water generated by industry, agriculture and local authorities, land stewardship, changes in agricultural practices);
- improving knowledge of the phenomenon and managing risks;
- restoring polluted environments through more effective cleaning and treatment techniques for washed-up algae.

ISSUES INVESTIGATED

On the basis of this green algae control plan, ANSES was requested to:

1. identify the complete spectrum of gases emitted by the algae and the corresponding risks to the health of exposed populations according to levels of concentration;
2. propose measurement and dosimetry protocols for sites affected by massive algae deposits;
3. review the scientific literature to seek information on potential health consequences that might be associated with chronic exposure to low hydrogen sulfide (H_2S) concentrations;
4. draw up specific recommendations for workers exposed while collecting and/or processing green algae;
5. draw up national recommendations on prevention for the general public and shoreline residents exposed to green algae emissions, depending on the potential toxicity thresholds and pollution, essentially olfactory in nature.

Given the urgent need of local decision-makers for the 2010 season, ANSES issued recommendations in July 2010 based on the currently available data, mainly intended for workers dealing with the collection of green algae. These recommendations, especially that the algae should be collected while still fresh, were intended to avoid most risk situations for those visiting the beaches or living nearby, or for workers (including seasonal workers) collecting the algae.

The shape of the coastline makes it difficult to access certain stretches, meaning that they can be cleared of algae only partially, or less frequently. These areas, where algae deposits can accumulate and decompose, create residual risk situations.

This health risk appraisal is intended to take these residual situations into account and to confirm and/or improve the recommendations issued in 2010, and possibly to add new ones.

SCOPE AND LIMITATIONS OF THE EXPERT APPRAISAL

The formal request was issued in the context of the green algae control plan drawn up for the period 2010-2015. It mainly concerns two species of algae (*Ulva armoricana* and *Ulva rotundata*) and the Brittany region. However, this expert appraisal and its conclusions may equally apply to any site affected by “green tides” of *Ulva* in other regions.

The industrial processing and its impact on the nearby population were not studied by ANSES as this is governed by the regulations covering classified facilities for environmental protection. The expert appraisal is not intended to replace those carried out

by operators but rather to produce general recommendations for the entire sector or for the monitoring of these facilities.

The Request concerned gases emitted by green algae into the atmosphere. Due to a lack of data, this study does not deal with biological aerosols or substances found in resulting from fermentation liquids, although this does not necessarily mean that exposure to these carries no health risk. Lastly, an appraisal of the direct effects on the flora, fauna and the environment and potential associated indirect effects on health are also outside the scope of this Request.

2. ORGANISATION OF THE EXPERT APPRAISAL

GENERAL ORGANISATION

This expert appraisal was carried out in accordance with the French standard NF X 50-110 "Quality in Expertise - General Requirements of Competence for Expert Appraisals (May 2003)".

The Agency set up a Working Group (WG) to investigate the issue and asked the Expert Committee (CES) on Assessment of the risks related to air environments to oversee the work carried out. In addition, the WG drew on skills from the Agency different units.

The methodological and scientific aspects of the work were regularly submitted by the Working Group to the CES, between 9 December 2010 and 19 May 2011. The report produced by the Working Group takes account of observations and additional information supplied by the members of the CES.

The first meeting of the WG was devoted to a number of interviews with stakeholders (central and local government departments, local authorities, local residents) in order to define as accurately as possible the issues and the objectives and scope of the Request. The WG also made visits to Brittany to see the beaches affected by green tides as well as the composting facilities for green algae. The WG was also able to meet local managers and voluntary associations.

PROCEDURES FOLLOWED BY THE EXPERTS

The scientific literature and the available results of measurement campaigns were examined for information about the emissions produced by green algae. As this revealed very little, a study was carried out in the summer of 2010 to characterise the spectrum of substances emitted by decomposing green algae as well as the kinetics of these emissions. Measurements were taken on a heap of green algae created *ex situ*. Screening for substances was directed at reduced sulfur compounds, ammonia (NH_3), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), aldehydes and volatile organic compounds (VOCs). The limited timeframe for dealing with the Request and the low quantities of green algae washed up in 2010 meant that only a narrow range of emission situations could be studied. The results therefore do not fully represent the potential variability.

The toxicological data for the substances emitted were taken from reference databases.

For the substances identified as having been emitted by green algae and considered to be toxic by inhalation, the standard method for health risk appraisal[1] was applied:

1. identification of hazards;

[1] NRC (1983) National Research Council, Committee on the Institutional Means for Assessment of Risks for Public Health. Risk Assessment in the Federal Government: managing the process, Nat. Acad. Press Washington

2. cataloguing and selecting dose-response relationships, validated by the ANSES Working Group on toxicity reference values (TRVs);
3. quantification of exposure, based on emission measurements *in situ* and *ex situ* as well as measurements from monitoring close to beaches;
4. risk characterisation.

■ MAIN LIMITATIONS AND UNCERTAINTIES

The available emission and exposure data do not seem to cover all exposure situations. Among other factors, they can depend on the thickness of algae deposits, the nature of the substrate, the ambient temperature and the rainfall. The lack of representativeness may mean that other exposure situations have not been characterised. Any attempt to extrapolate these findings, particularly regarding the kinetics of emissions and their corresponding risks, should therefore be made with the utmost prudence.

Due to the limited timeframe for the investigation, it was only possible to assess the health risks of a small number of substances. Furthermore, the substances were considered individually, without taking account of any potential "cocktail" effect of mixtures of different substances emitted by green algae, most of which are irritants.

Regarding risks to the health of workers involved in the collection, transport and processing of green algae, the little information available about exposure concerns only fresh algae. Beyond this, little is yet known about professional practices and, consequently, about the associated exposure scenarios.

3. ANALYSIS AND CONCLUSIONS OF THE CES

■ RESULTS

- **Characterisation of the spectrum of substances emitted into the air by green algae**

The scientific literature was found to contain very little on the nature and quantities of the substances emitted by green algae. As a result, characterisation of the spectrum is mainly based on the results of an *ex-situ* measurement campaign (reproduction of a heap of algae) carried out specifically for the purposes of this expert appraisal. To complete these findings, additional substances were included on the basis of hypotheses formulated by the experts. However, it is not possible to claim that the list of substances emitted (or suspected of being emitted) by green algae thus drawn up and presented in Table 1 is necessarily complete.

Table 1: List of substances emitted (or suspected of being emitted) into the air by green algae during decomposition

Substances observed during measurement campaigns		Suspected substances	
Name	**CAS number**	**Name**	**CAS number**
Hydrogen sulfide (H_2S)	7783-06-4	Sulfur dioxide (SO_2) *	7446-09-5
Dimethyl sulfide (DMS)	75-18-3	3-Dimethylsulfoniopropionate (DMSP)	7314-30-9
Methyl mercaptan	74-93-1	Acrylic acid	79-10-7
Dimethyl disulfide (DMDS)	624-92-0	Nitrous oxide (N_2O)	10024-97-2
Carbon disulfide (CS_2)	75-15-0	Acetic acid	64-19-7
Thioacetic acid	507-09-5	Lactic acid	50-21-5
Dimethyl sulfoxide (DMSO)	67-68-5	Sulfuric acid *	7664-93-9
Methanesulfonyl chloride	124-63-0	Sulfurous dioxide *	7782-99-2
Dimethyl trisulfide (DMTS)	3658-80-8	Ethanol	64-17-5
Dimethyl pentasulfide (DMPS)	7330-31-6	Acetamides	-
Dithiapentane	1618-26-4	Endotoxins	-
1,2,4-Trithiolane	289-16-7	* *suspected as traces*	
Dimethyl sulfone	67-71-0		
Ammonia (NH_3)	7664-41-7		
Urea	57-13-6		
Methane (CH_4)	74-82-8		
Acetaldehyde	75-07-0		
Formaldehyde	50-00-0		
Propionaldehyde	123-38-6		

During the discussions led by the CES concerning the work to characterise emissions, one expert also raised the possibility of the emission of phosphine (PH_3), whose toxicity is well documented, in view of the presence of phosphate. Such possible emissions could be investigated and characterised in future studies.

- **Emission kinetics**

Information on the kinetics of emissions during the decomposition of green algae was provided by the *ex situ* measurement campaign.

In the first few hours after the green algae are deposited on the beach:

- very low emissions of gas compounds produced by the algae decomposition process were recorded;
- with the exception of dimethyl sulfide (DMS) emitted naturally by green algae at very low concentrations, ammonia (NH_3) seems to be the only gaseous pollutant resulting from the degradation reaction.

In the next few hours:

- emissions of DMS increase significantly; furthermore, this is the only sulfur compound emitted in any significant quantity at this stage.

Over time, as the degradation of the green algae intensifies:

- other sulfur compounds appear (hydrogen sulfide [H_2S], methyl mercaptan, dimethyl disulfide [DMDS], dimethyl sulfoxide [DMSO] and carbon disulfide) whereas the quantities of dimethyl sulfide (DMS) diminish;
- concentrations of ammonia (NH_3) continue to increase, while remaining well below those of dimethyl sulfide (DMS);

- the decomposing algae also start to emit aldehydes.

These different phases of emissions can occur at different rates depending on a variety of criteria (temperature, rainfall, volume deposited by each tide, thickness of the deposit, abundance of microorganisms at the site, etc.). The first data available suggest that significant emissions of hydrogen sulfide (H_2S) commence between 12 and 48 hours after the algae is washed up.

- **Toxicity of the substances emitted by decomposing green algae**

For the situations studied (of exposure to emissions from green algae):

- The most frequently observed effects related to acute exposure by inhalation and associated with substances emitted by decomposing green algae are irritation of the respiratory mucosa and the eyes. At high concentrations, these irritations can lead to pulmonary oedema. Neurotoxic effects have also been described for several substances.
- The effects related to chronic exposure to be considered are mainly those associated with repeated exposure at concentration peaks. However, there have been very few studies on effects associated with this kind of exposure. Certain sequelae can result from specific conditions, such as depressed olfactory response caused by hydrogen sulfide (H_2S), but their clinical significance and duration have not been demonstrated in humans.

- **Health risk appraisal and provisional outlook**

It was only possible to make a quantitative appraisal for a very small number of substances as a result of the lack of TRVs and/or of exposure data. As a result, only acute health risks related to hydrogen sulfide (H_2S), ammonia (NH_3), formaldehyde and acetaldehyde, and chronic health risks related to hydrogen sulfide (H_2S) and ammonia (NH_3) underwent quantitative appraisal.

Regarding chronic risks for residents living close to beaches affected by green tides, massive deposits combined with insufficient collection can cause irritation and effects on the olfactory system due to hydrogen sulfide (H_2S). If the quantities of green algae deposited are not excessive or are removed frequently, there is little likelihood of these effects appearing.

The available occupational exposure data do not enable the appraisal of chronic health risks for workers involved in collecting, transporting and processing green algae.

Lastly, although the quantitative appraisal of acute health risks was carried out on the basis of emission data that therefore overestimated actual exposure, the results indicate that accidental situations involving for example the **breaking of the crust covering decomposing algae, or falling at a spot where putrefying algae has accumulated (e.g. mudflats), are potentially dangerous, especially as a result of hydrogen sulfide (H_2S) emissions**. These situations are a threat to workers and to the general population in equal measure.

For the first few hours after the arrival of these deposits, only small quantities of hydrogen sulfide (H_2S) are emitted by green algae, so that risk levels during this period are low. However, as the decomposition process intensifies (after a period that cannot be specified with certainty but which is estimated to be between 12 and 48 hours in view of the available data), exposure resulting from accidentally breaking the crust can reach levels that would probably induce effects such as irritation of mucous membranes of the eyes and respiratory tract as well as neurological symptoms. In extreme accidental cases, loss of consciousness and cardiac arrest or coma could result.

- **Main uncertainties regarding these results**

It should be remembered that few emission and/or exposure data are available and these probably do not cover the full range of emission conditions that can occur concerning the proliferation, tidal deposits and degradation of green algae. The unrepresentative nature of this information may mean that other exposure situations have not been characterised. Any attempt to extrapolate these findings, particularly regarding the kinetics of emissions and their corresponding risks, should therefore be made with the utmost prudence.

The conclusions of the health risk appraisal are also based on only partial knowledge of the risk, as only some substances were investigated, and then only individually. There has therefore been no appraisal of substances such as dimethyl sulfide (DMS) – even though it is emitted before hydrogen sulfide (H_2S), when the algae are still fresh, and in larger quantities – due to a lack of information about its toxic potential. Furthermore, other sulfur compounds, such as mercaptans, dimethyl disulfide (DMDS) and carbon disulfide (CS_2) could not be assessed despite their being emitted in large quantities.

Concerning the health risks for workers involved in the collection, transportation and processing of green algae, the rare exposure data available only concern fresh algae. Beyond this, little is yet known about professional practices and, consequently, the associated exposure scenarios are poorly characterised.

Lastly, it was not possible to characterise the effects of accumulated exposure to different substances emitted by green algae, most of which are irritants.

RECOMMENDATIONS FOR THE SAFETY OF WORKERS AND THE GENERAL POPULATION

The results of this expert appraisal support many of the recommendations published by ANSES in 2010, especially collecting green algae from beaches as early as possible. Considering the elements presented above, the main recommendations are to avoid the proliferation of algae and to limit exposure.

- **Avoiding the proliferation of green algae**

The experts reiterate the need to take measures to limit the proliferation of green algae, such as the reduction of nitrate inputs in the relevant watersheds. Risk situations due to masses of washed-up green algae would thereby be reduced automatically.

- **Avoiding exposure for the public**

To achieve this objective, some possible measures that could be deployed are suggested below.

- At present, **collecting green algae washed up on beaches as early as possible** is still the best way of reducing the toxic emissions related to their degradation and the associated risks. It is recommended that, when conditions allow (in terms of access, tide tables, etc.), **algae be collected, transported and treated in processing centres as rapidly as possible**. There are uncertainties concerning the best timetable for the collection of algae. It is impossible to determine from the available observations precisely when the fermentation gas emissions become significant. However, the data suggest that risk situations become inevitable after a period of 48 hours.
- Mark out collection areas. Setting up a collection site requires an appreciation of the specific risks of the time and place (geography, volume washed up, the way the deposit evolves, weather conditions) and the **signage** should take account of these

conditions. Marking should not only take account of the exposure of workers and the way the work is organised, but also the risks to local residents and visitors. Apart from permanent signage about the hazard, signs should be displayed temporarily during collection, with a view to keeping people away during operations. Any intermediary sites where algae are stored for draining before transport should also be indicated.

- Inform users, walkers and local residents of the dangers of **residual risk areas** (rocky stretches, mudflats) with permanent signage placed at points of access, as well as one-off or seasonal warning campaigns. This signage should also include information on the correct procedure to follow in the event of accidents. Lifeguards should also be trained to deal with this particular risk.
- Favour collection and processing procedures that limit the production and spread of gases, such as composting in closed containers.
- It would be useful to reinforce **environmental surveillance** with impromptu verifications, especially during the summer, of the atmospheric concentration of substances emitted by green algae, such as hydrogen sulfide (H_2S), around sites where green algae are processed.

- **Limiting the exposure of workers**

To achieve this objective, some possible measures that could be deployed are suggested below.

- **Personal gas monitors**. The technology behind these detectors, which involve electrochemical cells, requires regular verification, in workplace conditions and after every warning alarm, irrespective of manufacturer's instructions. It is also imperative that recommendations for storage be respected. In addition, it is recommended that manufacturers of personal gas monitors for hydrogen sulfide (H_2S) include in their instructions for use the concentrations of hydrogen sulfide (H_2S) at which they should be verified (for different ranges of concentration) together with information about possible interference with other products.
- **Green algae should be collected by mechanical means.** This method should be favoured whenever possible. The drivers' cabs of the machinery employed should provide sufficient protection from the atmospheric pollutants outside.
- When emission levels require the use of **personal respiratory protective equipment**, the filter unit offering the broadest protection against substances emitted by fresh and decomposing algae is ABEKP, Class 1 for gases and Class 3 for particles (i.e. A1B1E1K1P3). It is essential that these devices be kept in good working order and verified regularly.
- **Information and training**. Regulations governing hygiene and safety in the workplace include general provisions on the training of workers, especially including the use of personal protective equipment. In the case of algae, variations in the conditions under which the algae decompose and the multiplicity of associated risks, which vary over time, mean that it is necessary to keep information constantly updated and to provide specific training on risk appraisal, the benefits and specific aspects of the use of monitors, and the risks related to handling decomposing green algae. All workers involved in this process are concerned, irrespective of their contractual status, including seasonal workers. The training should also include emergency procedures in the event of acute intoxication.

- **The traceability of work involving exposure**. Traceability could be achieved using the medical records of workers concerned, irrespective of their status.

SUGGESTIONS FOR COMPLEMENTARY STUDIES AND THEMES FOR RESEARCH

Lastly, in the context of this study, the experts were faced with several limitations and uncertainties. These difficulties highlight the importance of acquiring new knowledge and performing complementary studies.

• Characterisation of emissions and exposures

Measurement campaigns could be continued with a view to improving knowledge of the spectrum of substances emitted (chemicals, endotoxins, mycotoxins, etc.) by green algae. Studies to identify and characterise any biological aerosols produced by deposits of green algae would also be worthwhile. Such campaigns should also attempt to provide more information about the influence of wind and terrain on the degree of ambient concentration as well as the influence of sunshine on gas emissions and their kinetics. In particular, this would help establish a maximum timeframe between tidal deposit and collection, to prevent the emissions from causing risk situations.

Considering the uncertainties surrounding the validity of extrapolating emission concentrations to exposure concentrations, any measurement campaign designed to better quantify exposure would be useful.

Too little is yet known about exposure of workers involved in collecting green algae. It is necessary to pursue these studies, especially those designed to assess the efficacy of filtering systems installed in the drivers' cabs of machinery for handling algae, as well as studies to improve knowledge concerning the chronic exposure of workers.

The relevance of monitoring the individual and collective exposure of exposed workers, e.g. via a cohort study, should also be investigated.

• Toxicity of the substances

There is so little information about the toxicity of certain substances, such as dimethyl sulfide (DMS) and thioacetic acid, despite their being emitted in large quantities, that it seems impossible to establish toxicity reference values (TRVs) for them. For these substances, the experts encourage research to acquire toxicity data, prior to establishing TRVs. For substances whose toxicity characterisation is more advanced, TRVs should be determined (dimethyl disulfide [DMDS] and methyl mercaptan).

Concerning endotoxins, the possibility that fermentation liquids could have irritant effects via endotoxins should be studied in order to remove the uncertainties apparent in the scientific literature currently available.

• Appraisal of biological and environmental risk

The microbiological risk related to biodegradation and any other routes of exposure could be assessed in their own right in order to complete the risk appraisal for all population groups. However, preventing degradation should also reduce other types of exposure that were outside the scope of this study.

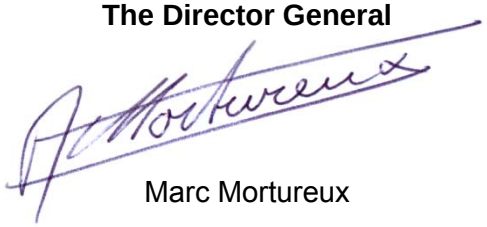
It would also be worthwhile to study risks to the environment in areas close to the decomposition of green algae.

4. THE AGENCY'S CONCLUSIONS AND RECOMMENDATIONS

The French Agency for Food, Environmental and Occupational Health & Safety endorses the conclusions and recommendations of its CES.

These conclusions and recommendations, resulting from the Committee's expert appraisal, supplement the provisions of the regulations covering classified facilities for environmental protection. It should be emphasised that sites where green algae are processed are generally such classified facilities and need to be legally declared and authorised, depending on the quantities of green algae processed. In the case of sites requiring authorisation, the operators of such facilities must carry out impact studies concerning the environment and the health of nearby residents. Care should be taken to ensure that a separate appraisal is performed for each facility, as laid down in current regulations.

The Director General



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KEYWORDS

Green algae, hydrogen sulfide, sulfur compound, gas, aerosol, air, risk appraisal, decomposition, putrefaction, fermentation.