Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22770

134 (2018) 128–134
December

Influence of body fluids compounds on trichloramine formation in swimming pool water

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Received 16 February 2018; Accepted 4 July 2018

ABSTRACT

The chlorine disinfectants are used to disinfect swimming pool water; in reaction with compounds dissolved in water, they cause the formation of many new substances, which are the disinfection by-products. Inorganic chloramines (mono-, di-, and trichloramine) also belong to this group of problematic substances. In a case of mono- and dichloramine, their negative effect on swimmers' health has not been observed; however trichloramine can cause skin and eye irritation, as well as cause inflammation of the airways, potentially also asthma. The article presents the dynamics of trichloramine formation from the nitrogen compounds that are introduced into the pool water along with body fluids such as urea, creatinine, glycine, histidine, arginine, uric acid, hippuric acid, and ammonia. Beside the individual human body fluids, their mixture and the sample of swimming pool water were also studied. These studies were conducted for 1–79 h. The research results showed that the dynamics of trichloramine formation differ for particular compounds. Urea, creatinine, ammonia as well as hippuric acid react slowly with chlorine; however trichloramine concentration in water remains at a similar level in up to 6 h. In the case of arginine, despite the rapid depletion of free chlorine, trichloramine concentration remained high up to 24 h of incubation. Glycine, histidine, and uric acid are precursors, for which trichloramine was formed with the highest rate in the first hour of observation, after which the concentration of both trichloramine and free chlorine dropped rapidly. The studies have shown the other compounds present in swimming pool water can reduce the reactivity of free chlorine, and in the consequence the smaller formation potential for trichloramine occurs.

Keywords: Disinfection by-products; Trichloramine; Swimming pool water

1. Introduction

The chlorine disinfectants are used to disinfect swimming pool water; in reaction with compounds dissolved in water, they cause the formation of many new substances, which are the disinfection by-products [1–4]. One of the parameters monitored by regulations and swimming pool water quality standards is combined chlorine. It is a kind of global parameter, because it includes inorganic and organic chloramines; however the amount of inorganic ones dominates [5]. Among the inorganic chloramines, three compounds are distinguished: mono-, di-, and trichloramine (NH_2Cl, $NHCl_2$, and NCl_3) [6,7]. In a case of mono- and dichloramine, their negative effect on swimmers' health has not been observed; however they can be the precursors of the other chlorination by-products, for example, nitrosamines, which are very harmful to health [8]. Scientific reports indicate that short exposure on trichloramine causes cough or irritation of the skin, eyes or airways, presumably also asthma. It can also cause changes in biomarkers in the lungs. However toxicological data on NCl_3 are really limited

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Presented at the 13th Conference on Microcontaminants in Human Environment, 4–6 December 2017, Czestochowa, Poland.

in the scientific literature [8–10]. Trichloramine is more volatile than other inorganic chloramines as well as organic by-products (it is four times more volatile than chloroform). Trichloramine easily transfers to the air of swimming pools, which is why inhalation is the predominant way of exposure for this compound [8,10,11]. Trichloramine is characterized by an irritating, strong fragrance, thus it is identified as a compound responsible for the specific, often irritating smell in the swimming pool, commonly misidentified to chlorine [10–13].

In swimming pool water, the concentration of combined chlorine is usually regulated by law, thus it is commonly measured. Combined chlorine concentration measured with N,N-diethyl-p-phenylenediamine (DPD) is commonly interpreted as inorganic chloramines in swimming pool water [6,7]. Individual chloramines are rarely monitored. The reported trichloramine concentration varies within a wide range of 7–1,500 μg/L [14]. When comparing the concentrations of inorganic chlorines in pool water, they are usually in the following order: $NH_2Cl > NHCl_2 > NCl_3$ [7].

The chloramine precursors are nitrogen-containing compounds that are introduced into the pool water by humans [15–17]. An average swimmer expels 25–30 mL of urine to pool water [18], but advanced swimmers 20–80 mL of urine and 0.1–1.0 L of sweat, during a 2-h training session [19]. Urea is the dominant pollutant among of the organic precursors [20]. An average amount of urea introduced by one person swimming for 2 h in a pool is 1.34 g [21]. Sweat and urine can also be the sources of other organic pollutants, such as creatinine, arginine, histidine, glycine [13,18,22,23], uric acid, hippuric acid, and citric acid [24,25]. Most of the compounds of human body fluids (HBF) contain nitrogen. It is assumed that a significant rate of trichloramine in swimming pool water is generated in the reaction of free chlorine with urea. Then, the trichloramine is hydrolyzed and forms mono- and dichloramine. In the next stage, mono- and dichloramine transform into the stable end products, including N_2 and NO_3^- [8,26]. In the most scientific publications, the degradation of urea by chlorine in pool conditions is defined as a very slow process [17,20]. Due to the lack of kinetic data on formation of NCl_3 from other nitrogen precursors, and in relation to reports which show the formation of this compound as the relatively fast process, some authors question the idea that the main source of trichloramine is urea, or generally the basic nitrogen fraction. Even if other nitrogen precursors present in water have significantly lower concentrations, their reactions with free chlorine can be much faster and thus contribute significantly to trichloramine formation [8,10].

The goal of the article is to study the dynamics of trichloramine formation from the nitrogen compounds that are introduced into the pool water along with HBF. The experiments were conducted under controlled laboratory conditions, using organic equivalents of HBF ingredients (urea, creatinine, glycine, histidine, arginine, uric acid, and hippuric acid), as well as inorganic ammonia. HBF mixture and the sample of swimming pool water were also studied. The dynamics of trichloramine formation were analyzed in 1–79 h.

2. Materials and methods

2.1. Preparation of precursors solutions

In order to examine the influence of the components of HBF introduced to water with swimmers on the trichloramine formation potential in chlorinated water, the following compounds were dissolved in ultrapure water: urea, creatinine, glycine, arginine, histidine, uric acid, hippuric acid (organic N-compounds), and inorganic ammonia. The concentration of all solutions was $1.8 \cdot \times 10^{-5}$ mol/L, as proposed by Weng and Blatchley III [22]. Table 1 presents basic information on the applied compounds.

In addition, the formation potential of a mixture of precursors was studied. Judd and Bullock [25] created the equivalent of HBF, including such organic nitrogen compounds as uric and hippuric acids, as well as citric acid, which does not contain nitrogen. Table 2 shows the composition of the mixture of HBF created by these authors.

The mixture was dissolved in ultrapure water at such a dilution that the ammonia concentration was $1.8 \cdot \times 10^{-5}$ mol/L (such as in the first stage of the experiment). However, swimming pool water is a mixture of not only compounds of the HBF, but also organic compounds from filling water, as well as epidermis, hair, saliva, and cosmetics. Therefore, the formation potential of trichloramine was determined for swimming pool water. Table 3 presents physicochemical characteristics of swimming pool water of the AGH swimming pool, from which the water sample was taken.

2.2. Trichloramine formation potential

The procedure of trichloramine formation potential for individual samples, disinfected with chlorine was adopted after Cimetiere and De Laat [27]. Prior the chlorination procedure, pH level in all analyzed solutions was adjusted to 7.00 ± 0.02 with the use of 1 M sulfuric acid or 1 M sodium hydroxide and 0.5 M phosphate buffer (5 mL buffer per each 250 mL of water). Concentration of free chlorine was adjusted to the level of 3.0 ± 0.2 mg/L, with sodium hypochlorite. The water samples were placed in dark glass bottles (250 mL) with a polytetrafluoroethylene septa. The bottles were incubated in the temperature of 25 ± 2°C. Due to the fact that the goal of the experiments was to study the dynamics of trichloramine formation, its concentration was determined for different incubation times, that is, every 1 h for the first 6 h, then after 24 h, 48 h, and 79 h. The whole procedure of the trichloramine formation potential test was carried out twice for each single sample (the presented results are an average from two results). Concentration of trichloramine was measured accordingly to DPD/potassium iodide method [28], with spectrophotometer Aurius 2021 UV-VIS by Cecil Instruments, United Kingdom. The detection limit for this method was 0.03 mg/L.

3. Results and discussion

Table 4 presents the average trichloramine concentrations obtained for all analyzed precursors and all incubation times.

3.1. Trichloramine formation potential for individual HBF

Fig. 1 shows the results of trichloramine concentration, which were obtained in its formation potential test (NCl_3–FP) for organic precursors (Figs. 1(a)–(g)) and ammonia (Fig. 1(h)). The results of residual-free chlorine concentration are also shown in the figure.

Table 1
Physicochemical properties of compounds used in experiments (information from manufacturers

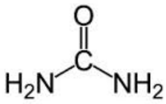
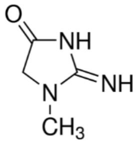
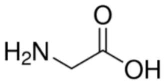
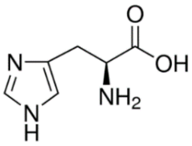
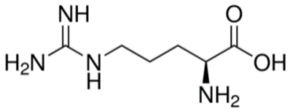
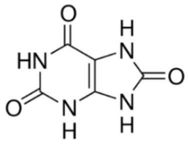
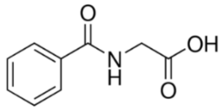
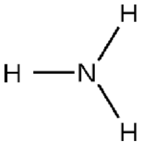
Compound	Structural formula	Molar mass, g/mol	Concentration	Manufacturer
Urea		60.06	minimum 99.8%	Avantor (Poland)
Creatinine		113.12	>99%	Acrōs Organics (Belgium)
Glycine		75.07	>99%	Acrōs Organics
Histidine		155.15	98%	Acrōs Organics
Arginine		174.2	>98%	Acrōs Organics
Uric acid		168.11	>99%	Acrōs Organics
Hippuric acid		179.17	98%	Acrōs Organics
Ammonia		17.031	25%	Avantor

Table 2
Composition of the mixture simulating the human body fluids [25]

Ingredient/compound	Concentration, mg/L	Organic carbon[a], mg/L	Nitrogen, mg/L
Ammonium chloride	2,000	–	520
Urea	14,800	2,960	6,900
Histidine	1,210	560	320
Hippuric acid	1,710	1,040	134
Uric acid	490	180	160
Citric acid	640	240	–
NaH_2PO_4	4,300	–	6–9
Creatinine	1,800	770	67

[a] 96%–98%.

As the results of the studies on the dynamic behavior of trichloramine have shown, it differs for individual precursors. Glycine (Fig. 1(c)), histidine (Fig. 1(e)), and uric acid (Fig. 1(f)) react with chlorine very rapidly. After 1 h of incubation with these precursors, trichloramine concentration was highest and was 0.39 mg/L, 0.21 mg/L, and 0.19 mg/L, respectively, for glycine, histidine, and uric acid. Then, in following hours of observation, trichloramine concentration decreased. It was caused by the decrease in residual-free chlorine content, which quickly disappeared in these samples. Despite the rapid decrease of residual-free chlorine concentration in the sample with arginine (Fig. 1(d)), trichloramine concentration was relatively high within the whole observation period (average 0.65 mg/L, from 0.37 mg/L for 48 h incubation to 0.87 mg/L for 3 h incubation), and it was the highest of all analyzed precursors. Generally, trichloramine is one of many by-products formed in the reaction of chlorine with the compounds introduced with HBF. However, according to the research report by Li and Blatchley III [13], which besides NCl_3 was studying also the formation of $CNCHCl_2$ and CNCl, trichloramine was the only disinfection by-product, which was formed in reaction with arginine.

For the other analyzed precursors, that is, urea (Fig. 1(a)), creatinine (Fig. 1(b)), hippuric acid (Fig. 1(g)), and ammonia (Fig. 1(h)) NCl_3 formation had the same dynamics.

Table 3
Physicochemical parameters of swimming pool water

Parameter	Concentration
N_{NH4}, mg/L	0.09
N_{NO2}, mg/L	<0.002
N_{NO3}, mg/L	4.80
Total nitrogen, mg/L	5.00
Dissolved organic carbon, mg/L	3.28
Specific ultraviolet absorbance, m^{-1}•L/mg	1.128
Br^-, mg/L	0.43
pH	7.02
Conductivity, mS/cm	2.27

The formation of NCl_3 was slow and its concentration remained at a relatively stable level until the sixth hour of observation. After 24 h reaction time, the reaction of residual-free chlorine dropped and a slight decrease in trichloramine concentration occurred as well. The average NCl_3 concentration for these precursors was as follows: 0.38 mg/L for urea, 0.26 mg/L for creatinine, 0.25 mg/L for hippuric acid, and 0.32 mg/L for ammonia. It indicates that the most of precursors form trichloramine in the first hours of the reaction, which is a confirmation of the assumptions of Soltermann et al. [8] that, apart from urea, other precursors introduced into swimming pool water with HBF, despite their lower concentration, can significantly contribute to the trichloramine formation in water. To assess the reactivity of precursors in relation to the disinfection by-products formation, longer reaction times are often examined. Due to Li and Blatchley III [13] in a 24-h reaction period, the most detectable changes in water chemistry have been completed. However, analyzing the trichloramine formation potential for individual precursors only after 24 h, the influence of glycine, histidine, and uric acid on the formation of this compound would be difficult to detect.

Ammonium ions, urea, and creatinine, and in a lower extent α-amino acids (glycine), histidine, glycine, and arginine have been described as trichloramine precursors [10,13]. The mechanism of trichloramine formation is based on a simple substitution with Cl^+. The most of organic amines (e.g., urea), including primary, secondary, and tertiary amines, may be the trichloramine formation precursors. In a case of creatinine, the mechanism of forming trichloramine begins with substitution with chlorine, followed by hydrolysis with forming urea (among the other substances), which is a precursor of trichloramine formation. Thus trichloramine can be formed as a result of chlorination of precursors present in swimming pool water, but also as a result of the transformation of other chlorination by-products formed in this environment, for example, by reaction of dichloroacetonitrile with free chlorine [13].

3.2. *Trichloramine formation potential of the precursors mixture*

Swimming pool water is a mixture of many ingredients dissolved in water, and the trichloramine formation may

Table 4
The trichloramine formation potential from human body fluids components

Compound	Trichloramine formation potential, mg/L								
	1 h	2 h	3 h	4 h	5 h	6 h	24 h	48 h	79 h
Urea	0.56	0.57	0.59	0.35	0.35	0.21	0.31	0.29	0.23
Creatinine	0.30	0.29	0.39	0.30	0.30	0.20	0.25	0.18	0.10
Glycine	0.39	0.12	0.09	0.09	0.09	0.05	nd	nd	nd
Arginine	0.70	0.76	0.87	0.62	0.62	0.83	0.66	0.37	0.43
Histidine	0.21	0.08	nd	nd	nd	0.04	0.04	nd	nd
Uric acid	0.19	0.16	0.04	0.03	0.03	nd	0.03	nd	nd
Hippuric acid	0.36	0.18	0.29	0.34	0.34	0.20	0.18	0.17	0.16
Ammonia	0.33	0.46	0.33	0.44	0.44	0.41	0.20	0.12	0.13
HBF mixture	0.16	0.57	0.14	0.22	0.22	0.17	0.25	0.28	0.17
Swimming pool water	0.26	0.27	0.29	0.28	0.28	0.44	0.70	0.14	0.07

nd, not detected.

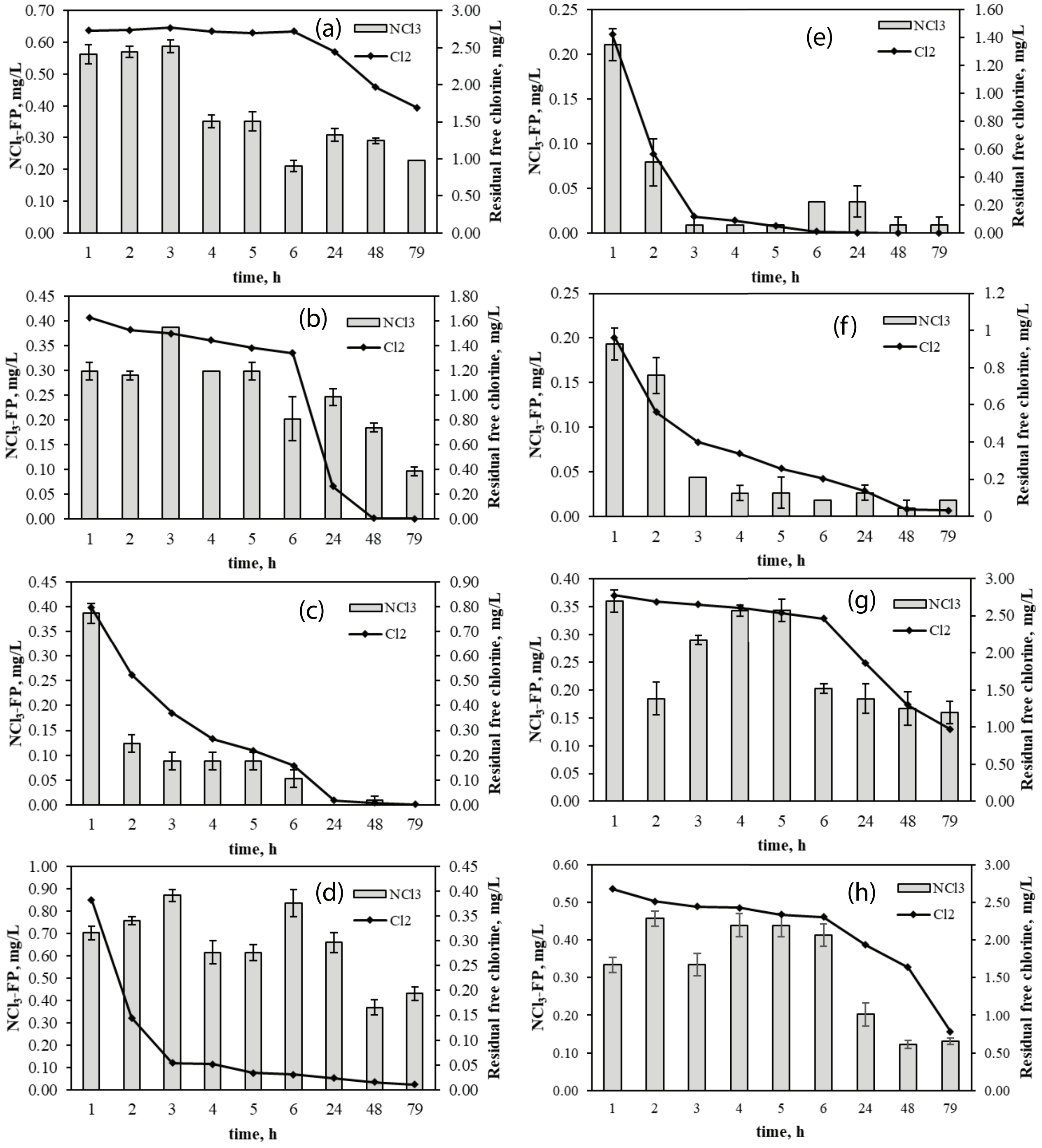


Fig. 1. Trichloramine formation potential (pH 7, 25°C) and residual free chlorine concentration (Cl_2) for (a) urea, (b) creatinine, (c) glycine, (d) arginine, (e) histidine, (f) uric acid, (g) hippuric acid, and (h) ammonia.

proceed in a slightly different way. Fig. 2 shows the formation potential of trichloramine from an HBF mixture (Fig. 2(a)) and pool water (Fig. 2(b)).

The formation of trichloramine in HBF mixture was different than in samples with the individual components of HBF. The maximum concentration of trichloramine was observed in 2 h observations (0.57 mg/L) and then the concentration dropped to 0.14 mg/L in 3 h of the experiment. In the following hours, the trichloramine concentration slightly increased, reaching a level of 0.28 mg/L in 48 h, after this time a drop in trichloramine concentration to 0.17 mg/L was observed in 79 h.

In the swimming pool water sample, the formation potential of trichloramine increased from a concentration of 0.26 mg/L in 1 h of observation to 0.70 mg/L in 24 h. After reaching the maximum, a sharp decrease in trichloramine

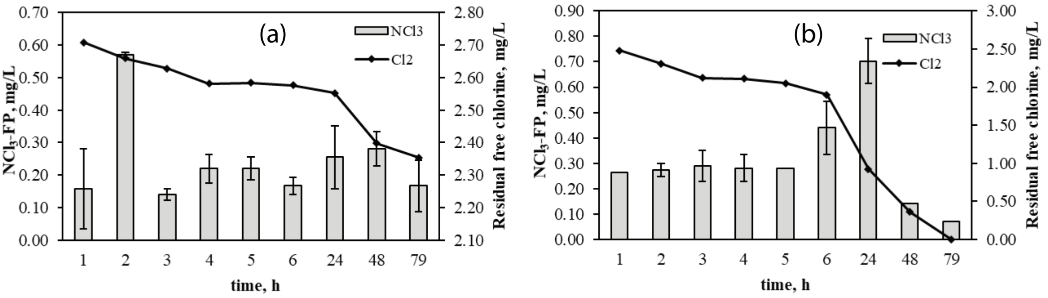


Fig. 2. Trichloramine formation potential (pH 7, 25°C) and residual free chlorine concentration (Cl_2) for (a) mixture of human body fluids and (b) swimming pool water.

concentration was observed – 0.14 and 0.07 mg/L in 48h and 79 h of experiment, respectively. This was caused by the decrease of the free chlorine concentration.

Comparing the obtained results for the formation potential of trichloramine from the mixture of precursors with those obtained from the individual HBF, it can be observed that this potential is lower when there is a larger amount of components in the sample. This phenomenon was also observed by other authors. The potential for forming disinfection by-products of the sum of isolated fractions is smaller than their mixtures [29,30]. It is explained by the fact that other components of water can reduce reactivity of residual chlorine, which in turn causes the less intensive formation of disinfection by-products.

4. Conclusions

Dynamics of trichloramine formation in swimming pool water are not fully understood. Some discrepancies in scientific literature, and generally the imprecision and limited amount of existing research reports, cause this issue requiring future studies and deep examination. The research presented in this article confirmed that trichloramine is formed from precursors introduced along with HBF into swimming pool water. The dynamics of trichloramine formation differ for individual examined compounds. Urea, creatinine, ammonia as well as hippuric acid react slowly with chlorine; however trichloramine concentration remains at a similar level in up to 6 h. In the case of arginine, despite the rapid consumption of free chlorine, trichloramine concentration remained at a high level up to 24 h of incubation. Glycine, histidine, and uric acid are precursors, for which the highest trichloramine concentration was observed at the first hour of observation, after which the concentration of trichloramine and free chlorine dropped rapidly. However, the trichloramine concentration in swimming pool water was not as high as if it would result from the sum of its formation by individual components. The other ingredients found in pool water can reduce the reactivity of free chlorine, and in a consequence decrease the formation potential of trichloramine.

Acknowledgment

The work was completed under AGH University of Science and Technology statutory research for the Department of Environmental Management and Protection.

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